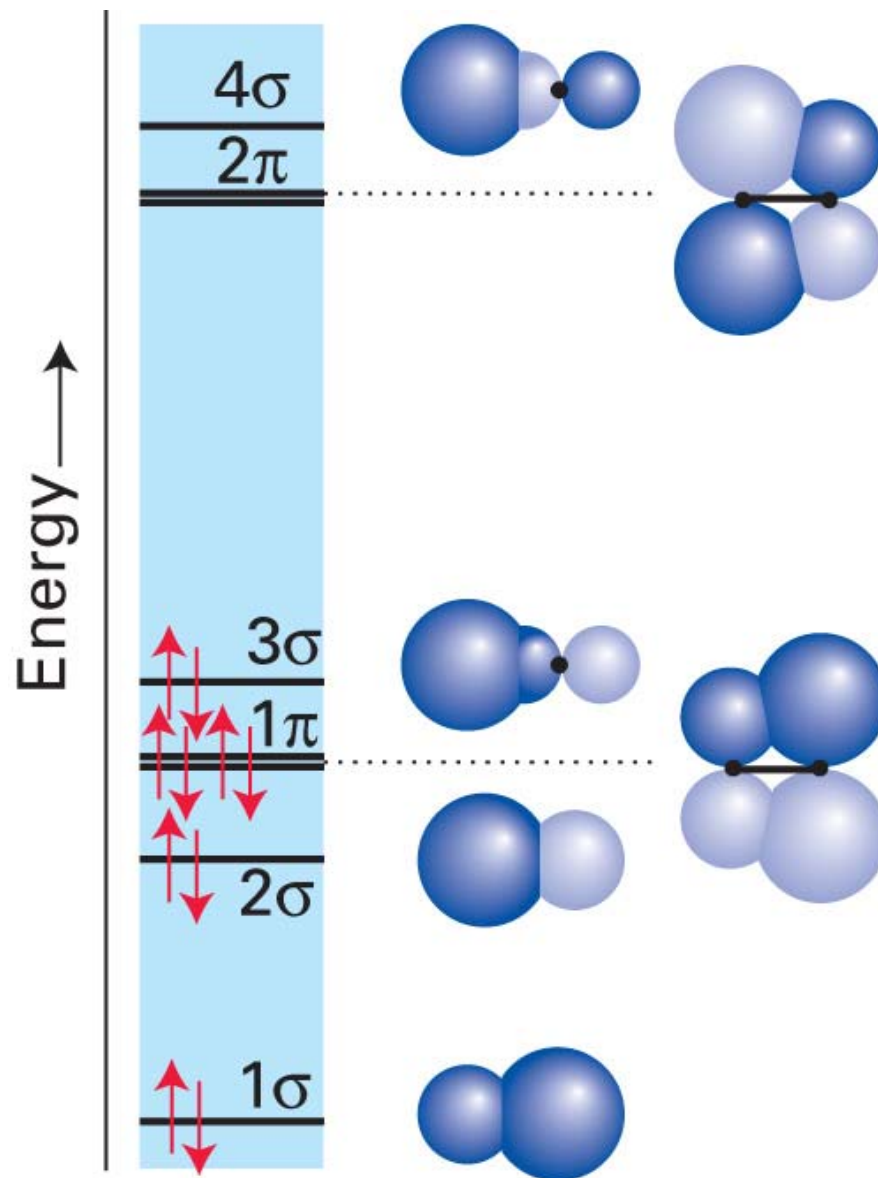
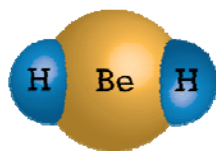


# Lecture 17 MO Theory

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

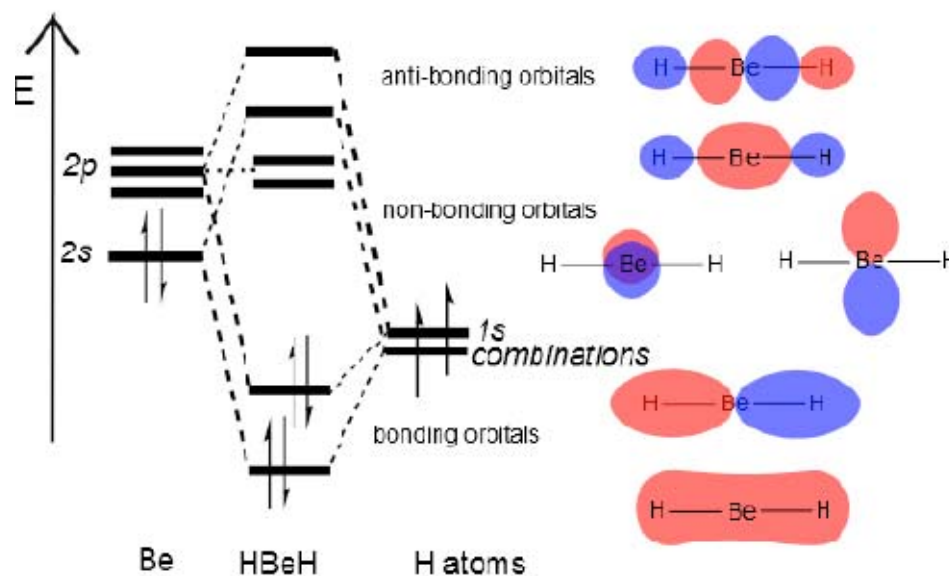
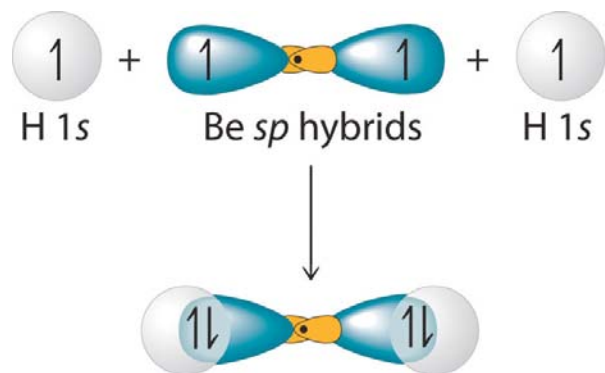
# *MO's for CO: the contour plots and significance for Metal Carbonyls*



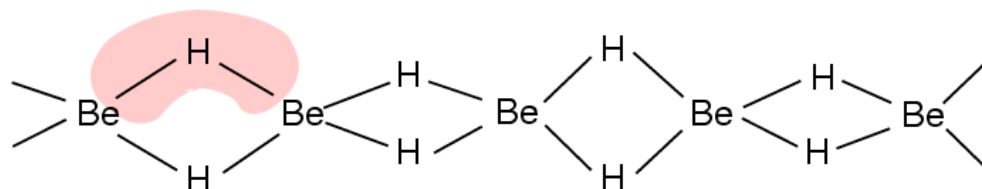


## Molecular Orbitals

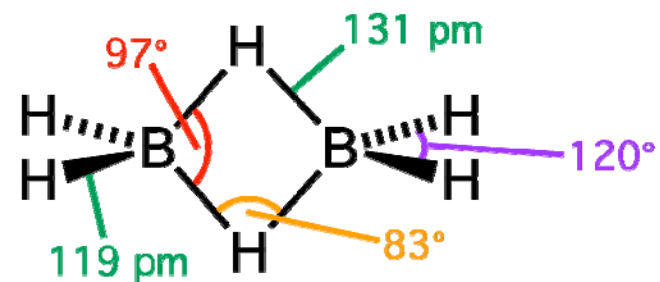
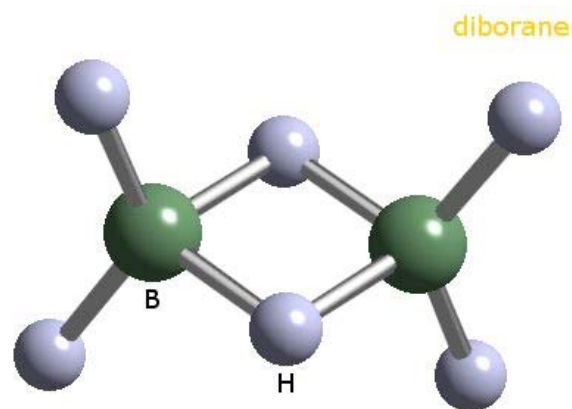
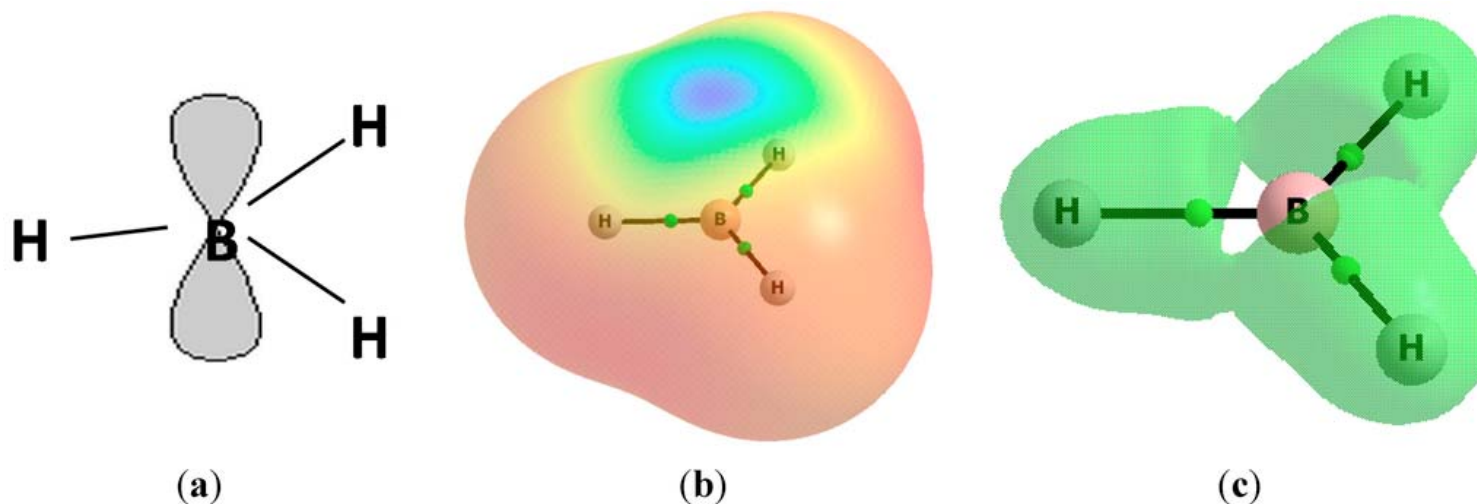
Localized or Valence Bonds:



Electron Deficiency leads to aggregation via a bridging hydride

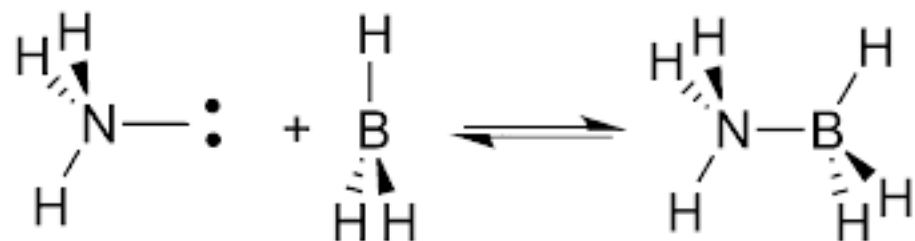


*Electrophilic center in  $BH_3$  accounts for its more stable structure as dimer, diborane*

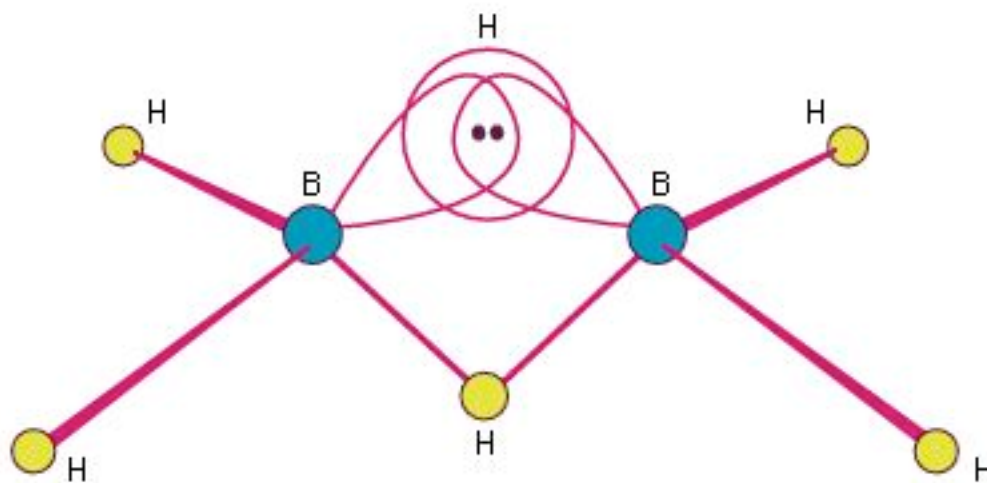


$BH_3$  dimerizes with 3-centered, 2-electron bond; in diborane, each B considered to be  $sp^3$  hybrid— a quasi tetrahedron.

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



$$K = \frac{[\text{NH}_3\text{-BH}_3]}{([\text{NH}_3][\text{BH}_3])} \sim 10^{55}$$

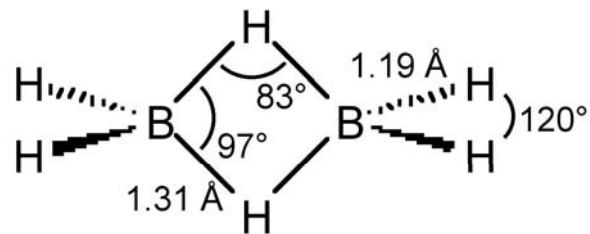
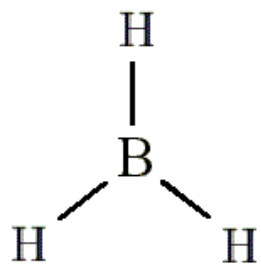


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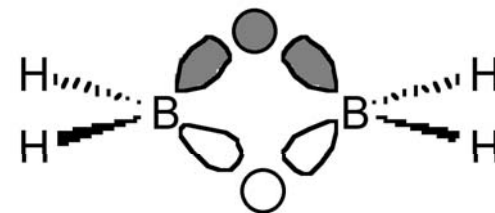
Describe Bridge bond by a combination of hybrid orbitals and delocalized MO's.

Bond angles	Spatial geometry	Electron pair geometry	Lone pair substitutions				
180°	 Linear	 ( <i>sp</i> )	...			$s + p_z$	
120°	 Trigonal planar	 ( <i>sp</i> <sup>2</sup> )	 Bent			$s + p_x + p_y$	
109.5°	 Tetrahedral	 ( <i>sp</i> <sup>3</sup> )	 Trigonal pyramidal	 Bent			$s + p_x + p_y + p_z$
90°, 120°	 Trigonal bipyramidal	 ( <i>dsp</i> <sup>3</sup> )	 "Sawhorse"	 T-shaped	 Linear	$(s + p_x + p_y) + (p_z + d_{z^2})$	
90°	 Octahedral	 ( <i>d</i> <sup>2</sup> <i>sp</i> <sup>3</sup> )	 Square pyramidal	 Square planar	 T-shaped	 Linear	$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$

## Lessons from Borane: $\text{BH}_3$ and $\text{B}_2\text{H}_6$

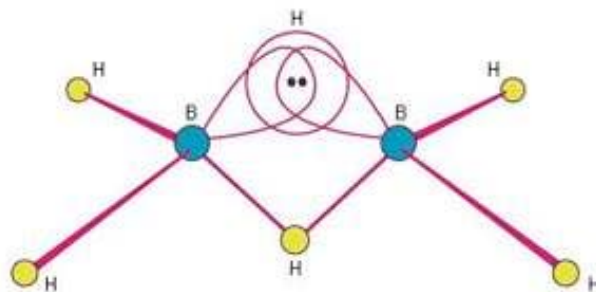


(a)

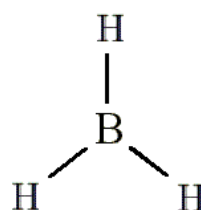


(b)

Terminal hydrides;  
Bridging hydrides



Electron Deficient



$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$		
$A_1'$	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	$(R_x, R_y)$	$(xz, yz)$