

LECTURE 21/36

OCTOBER/20/02

— POLY ATOMIC MOLECULES

BACKGROUND: OKOBY CH 16

READ: TODAY'S LEC GRAY CH 4  
p104-119

NEXT LEC GRAY CH 4  
p120-135

## WAVE FUNCTIONS FOR POLYATOMIC MOLECULES

DELOCALIZED ELECTRONS  $\leftrightarrow$

UNHYBRIDIZED ATOMIC ORBITALS

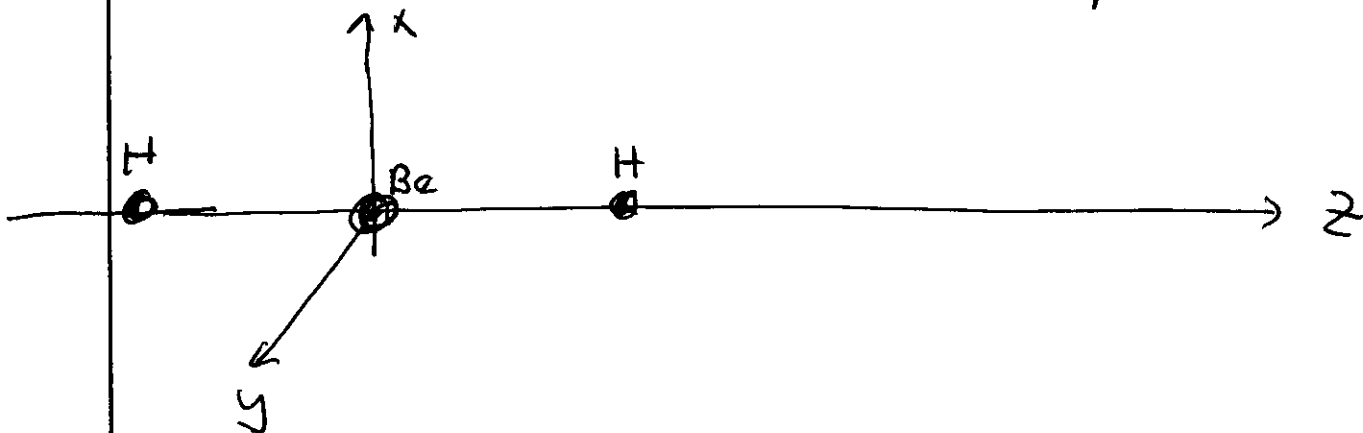
LOCALIZED ELECTRONS  $\leftrightarrow$

HYBRIDIZED ATOMIC ORBITALS  $sp, sp^2, sp^3$   
 $sp^3d, sp^3d^2$

Be H<sub>2</sub>

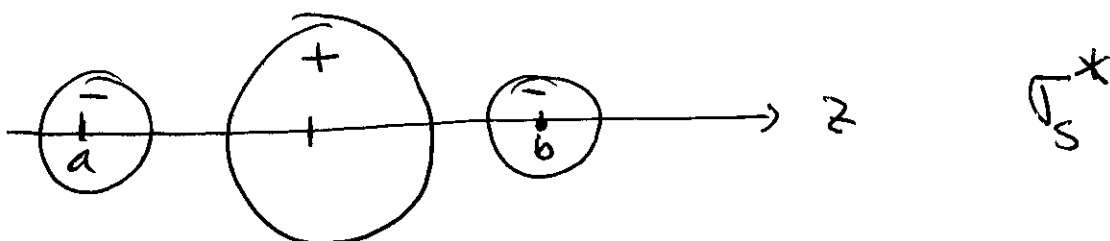
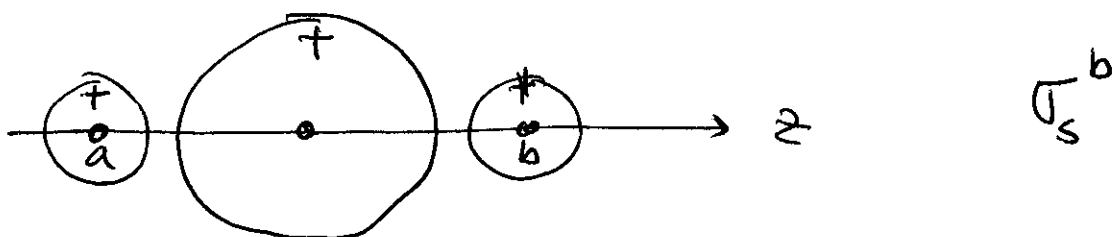
FROM H WE HAVE 1S ELECTRONS, AND

FROM Be WE HAVE 2S AND 2P ORBITALS



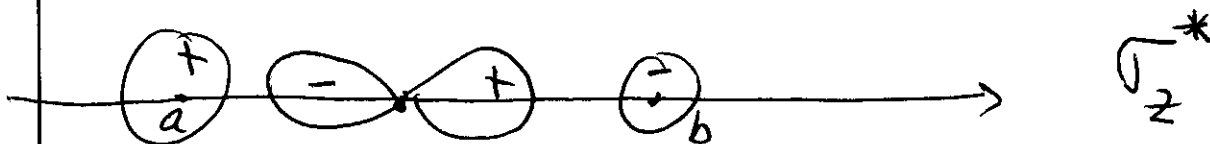
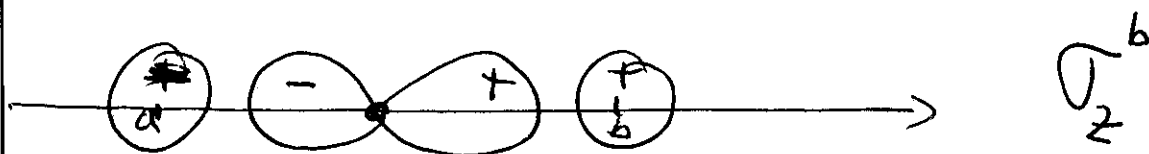
SINCE WE CHOSE THE Z DIRECTION ALONG THE AXIS OF THE MOLECULE, WE

CAN ONLY MIX THE 2S WITH THE 1S  
AND 2P<sub>z</sub> WITH THE 1S ORBITALS.



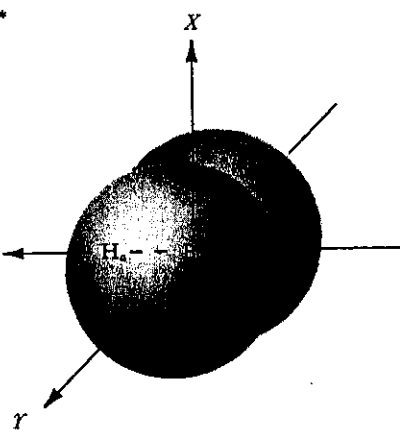
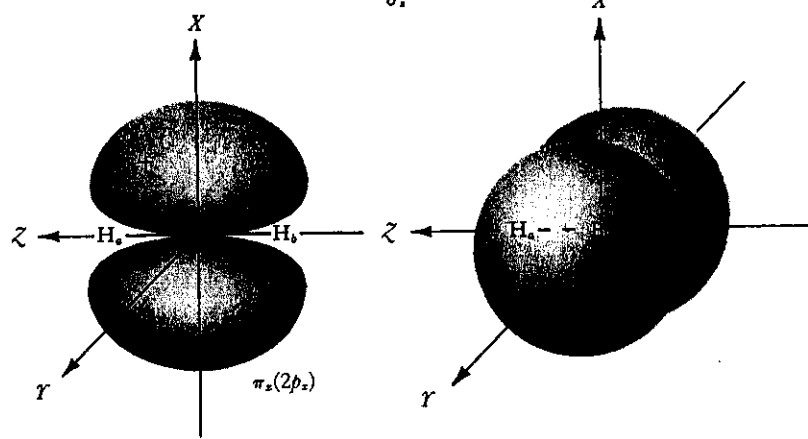
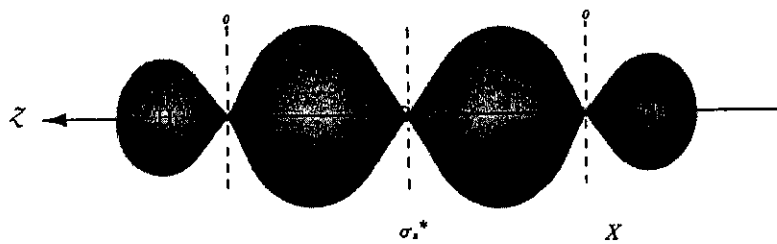
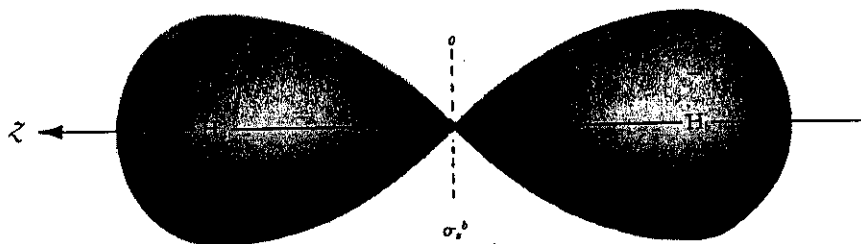
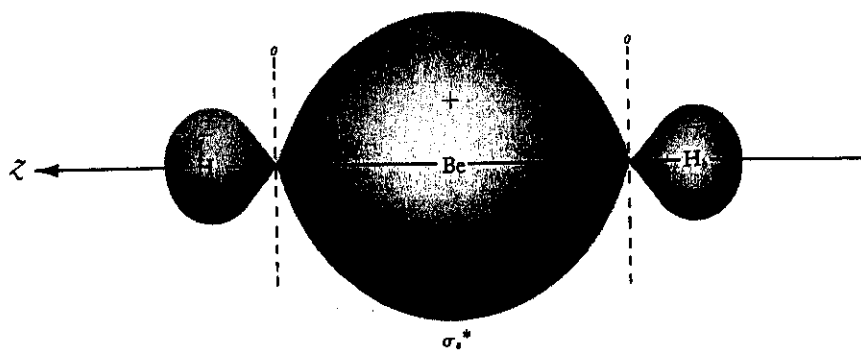
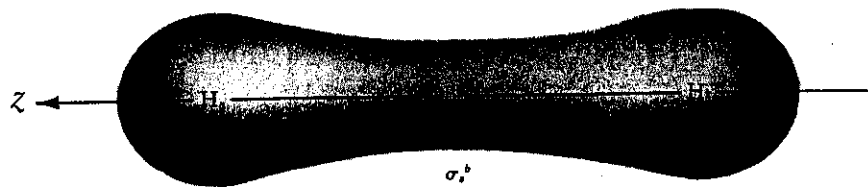
$$\sigma_s^b \propto 2s + \lambda_1 (1s_a + 1s_b)$$

$$\sigma_s^* \propto 2s - \lambda_1' (1s_a + 1s_b)$$



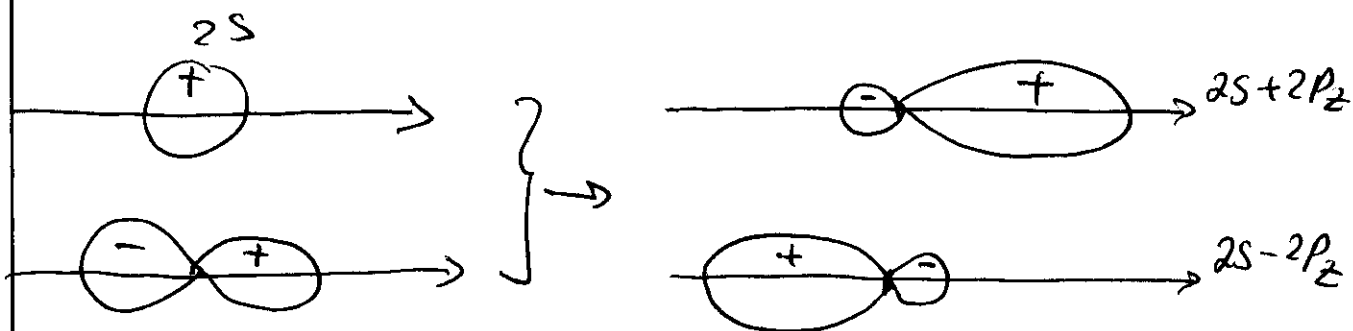
$$\sigma_z^b \propto 2p_z + \lambda_2 (-1s_a + 1s_b)$$

$$\sigma_z^* \propto 2p_z + \lambda_2' (1s_a - 1s_b)$$

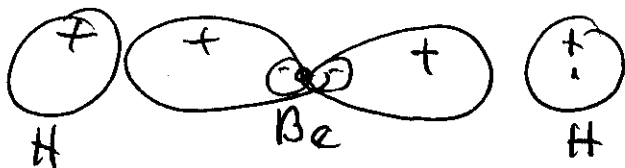


## LOCALIZED MO

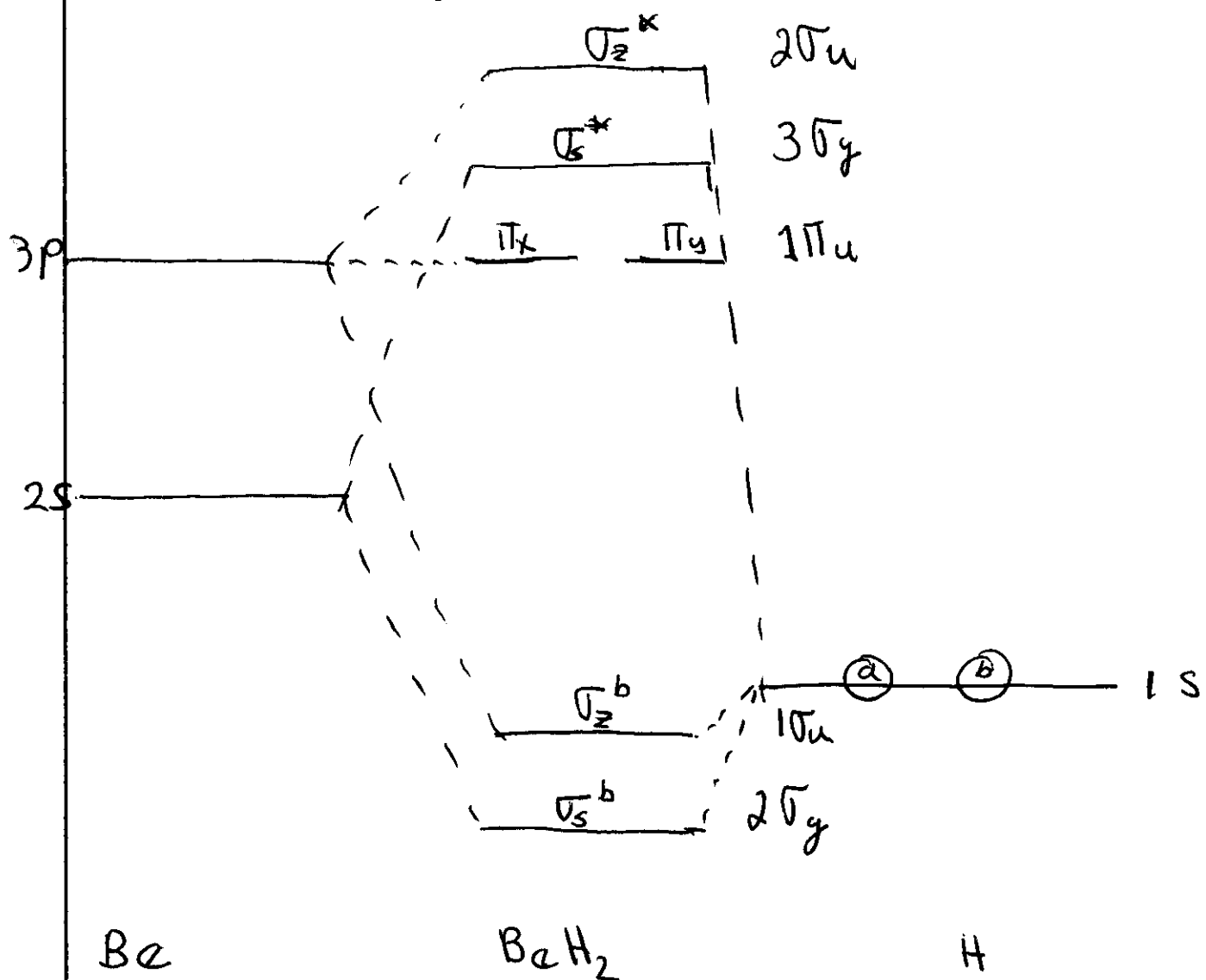
IN THIS METHOD WE HYBRIDIZE THE 2S AND 2P<sub>z</sub> ORBITALS AND GET 2 EQUIVALENT SP HYBRID ORBITALS DIRECTED ALONG THE z AXIS.



EACH OF THESE ORBITALS CAN BE USED TO FORM A LOCALIZED MO



THE  $2p_x$  AND  $2p_y$  ARE NON BONDING  
 BE ORBITALS,  $\pi_x$  AND  $\pi_y$ .



GROUND STATE

$$(1s)^2 (\sigma_g^b)^2 (\sigma_u^b)^2$$

$$(\pi_u)^2 (2\sigma_g)^2 (1\sigma_u)^2$$

$1s$  OF  $\text{Be}$  IS NON BONDING



WE NEED 3 bonding HYBRID ATOMIC ORBITALS. IN THIS CASE WE COMBINE THE 2S AO WITH TWO 2P ORBITALS. THE CHOSEN 2P ORBITAL DEFINE A PLANE. THE PREDICTED STRUCTURE IS TRIGONAL PLANAR

$$\psi_1 = \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z$$

$$\psi_2 = \frac{1}{\sqrt{3}} 2s - \frac{1}{\sqrt{6}} 2p_z + \frac{1}{\sqrt{2}} 2p_x$$

$$\psi_3 = \frac{1}{\sqrt{3}} 2s - \frac{1}{\sqrt{6}} 2p_z - \frac{1}{\sqrt{2}} 2p_x$$

THE ANGLE BETWEEN THESE BONDING AO IS  $120^\circ$ ; WHICH DEFINES THE ANGLE BETWEEN H-B-H IN  $BH_3$

## CH<sub>4</sub> METHANE

IN THIS CASE WE COMBINE THE 2S AO WITH THE 3 2P AO  $\Rightarrow$  4 sp<sup>3</sup> HYBRID AO.

$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

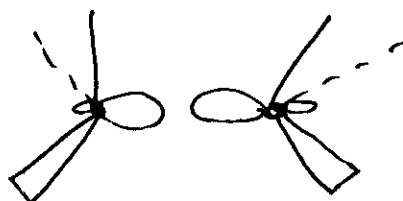
$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

THESE ORBITALS POINT TOWARDS THE VERTICES OF A TETRAHEDRON, WITH ANGLE BETWEEN ORBITALS OF 109.5°

## C<sub>2</sub>H<sub>6</sub> ETHANE





THE COMBINATION OF A HYBRID AO  
AND A 1S AO (H) GIVES A  
LOCALIZED  $\sigma$  MO.

EXPERIMENT

NEUTRON DIFFRACTION  $\text{CH}_4$  H-C-H ANGLE  $109' 28''$   
C-H BOND LENGTH  
 $1.093 \text{ \AA}$



IN THIS CASE WE COULD USE THE DELOCALIZED MO METHOD AND PLACE  $2e^-$  IN THE 2S ORBITAL AND AND FORM DELOCALIZED MO (3) WITH THE 3 2P ORBITALS. THUS WE PREDICT AH-N-H ANGLE OF  $90^\circ$ .

IN CONTRAST THE LOCALIZED MO METHOD HYBRIDIZES THE 2S AND THE 3 2P ORBITALS. SO WE CAN USE 3 ( $sp^3$ ) ORBITALS FOR BONDING AND PLACE THE LONE  $e^-$  PAIR IN THE FOURTH  $sp^3$  ORBITAL. THEREFORE, WE PREDICT A H-N-H ANGLE OF  $109.5^\circ$ . THE EXPERIMENTAL ANGLE IS  $107^\circ$ . (REPULSION OF THE VALENCE  $e^-$ S IS IMPORTANT IN DETERMINING THE STRUCTURE