

# Hybridized Orbitals

CHEM 361B: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry  
California State University, Fullerton

Lecture 17

# Table of contents

## 1 Orthogonal Wavefunctions

## 2 Hybridised Orbitals

- sp Orbitals
- $sp^2$  Orbitals
- $sp^3$  Orbitals

### Learning Objectives:

- Mix wavefunction solutions for s and p orbitals to predict the geometry of hybridised orbitals

### References:

- Engel and Reid §24.1 - §24.4

# Orthogonal Wavefunctions

For two nondegenerate states, they are said to be orthogonal if

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = 0 \quad \text{for } m \neq n$$

For instance, different states of a particle in a box are orthogonal.

$$\frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx = 0 \quad \text{for } m \neq n$$

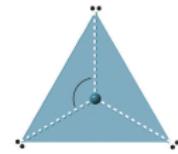
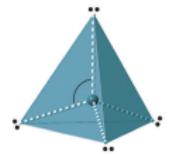
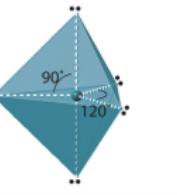
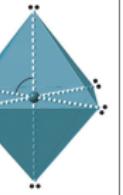
This same principle applies to spin states

$$\int \alpha^* \beta d\sigma = \int \beta^* \alpha d\sigma = 0$$

# Valence shell electron pair repulsion (VSEPR) theory

VSEPR is a qualitative model based on observable electron densities which can predict the structure of many molecules.

- The electrons around the central atom (bonding and non-bonding) repel each other so the minimum energy geometry minimizes these repulsions

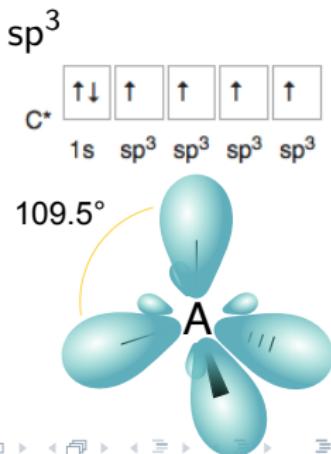
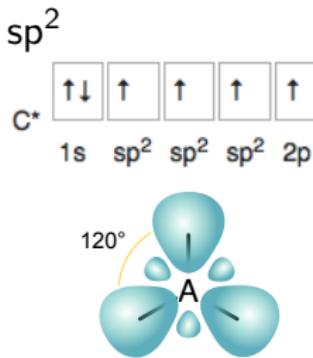
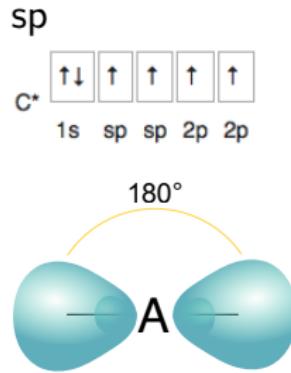
Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
					
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

# Hybridised Orbitals Overview

Predicting bond angles using Molecular Orbitals is not straightforward. Instead, the atomic orbitals around a central atom can be mixed into hybridised orbitals. Fx. Carbon has 6 electrons:



Its atomic orbitals can be hybridised into



# Hybrid Orbitals - sp

Consider BeH<sub>2</sub>. The two Be-H bonds are

- Equivalent
- 180° from each other

Be has a ground state electron configuration of (1s)<sup>2</sup>(2s)<sup>2</sup>. To get the directionality of the two Be-H bonds, take a linear combination of the Be 2s and 2p<sub>z</sub> orbitals

$$\xi_1 = a_1 2s_{Be} + b_1 2p_{zBe}$$

$$\xi_2 = a_2 2s_{Be} + b_2 2p_{zBe}$$

One electron in the Be 2s orbital is promoted to the 2p<sub>z</sub> orbital to form two bond orbitals between Be and H<sub>A</sub> and H<sub>B</sub>

$$\psi_1 = c_1 1s_A + c_2 \xi_1$$

$$\psi_2 = c_3 1s_B + c_4 \xi_2$$

# Hybrid Orbitals - sp

To determine the constants from  $\phi_1$  and  $\phi_2$  start with the approximate orbitals for beryllium

$$\psi_{2s} = \left( \frac{1}{4\pi} \right)^{1/2} R(r)$$

$$\psi_{2p_z} = \left( \frac{3}{4\pi} \right)^{1/2} R(r) \cos \theta$$

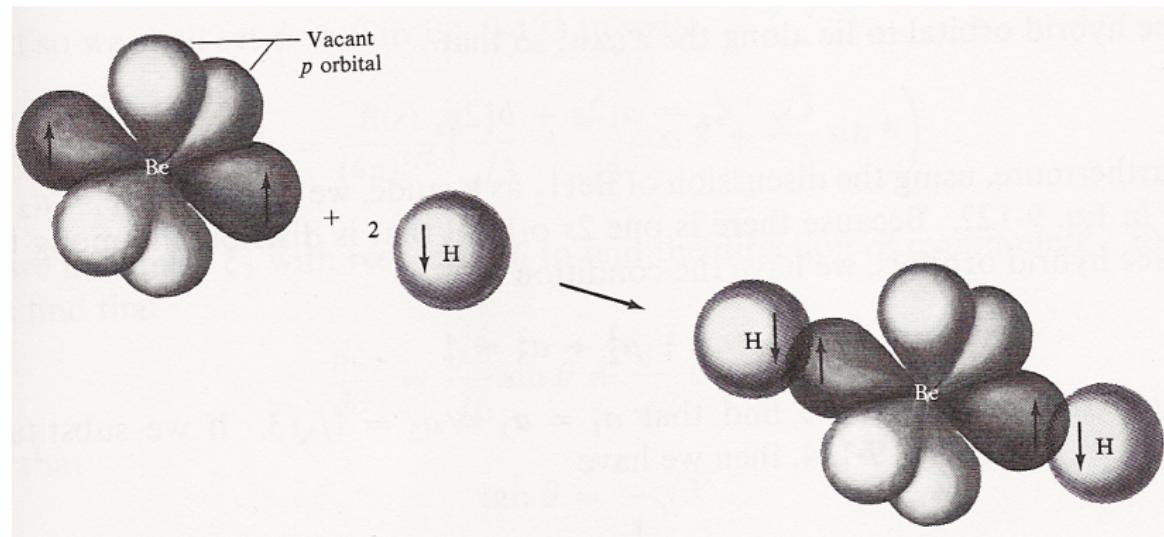
which, after applying normalization and orthogonalization conditions gives

$$\xi_1 = \frac{1}{\sqrt{2}} (2s_{Be} + 2p_{zBe})$$

$$\xi_2 = \frac{1}{\sqrt{2}} (2s_{Be} - 2p_{zBe})$$

This shows that the two hybrid orbitals are 180° from each other

# Hybrid Orbitals - sp



# Hybrid Orbitals - sp<sup>2</sup>

Consider the molecule BH<sub>3</sub>. The three B-H bonds are equivalent and lie in a plane directed 120° from each other. To describe the three equivalent bonds first construct the three hybrid orbitals on the boron atom using the 2s, 2p<sub>z</sub> and 2p<sub>x</sub> (where x is chosen arbitrarily)

$$\xi_1 = a_1 2s + b_1 2p_z + c_1 2p_x$$

$$\xi_2 = a_2 2s + b_2 2p_z + c_2 2p_x$$

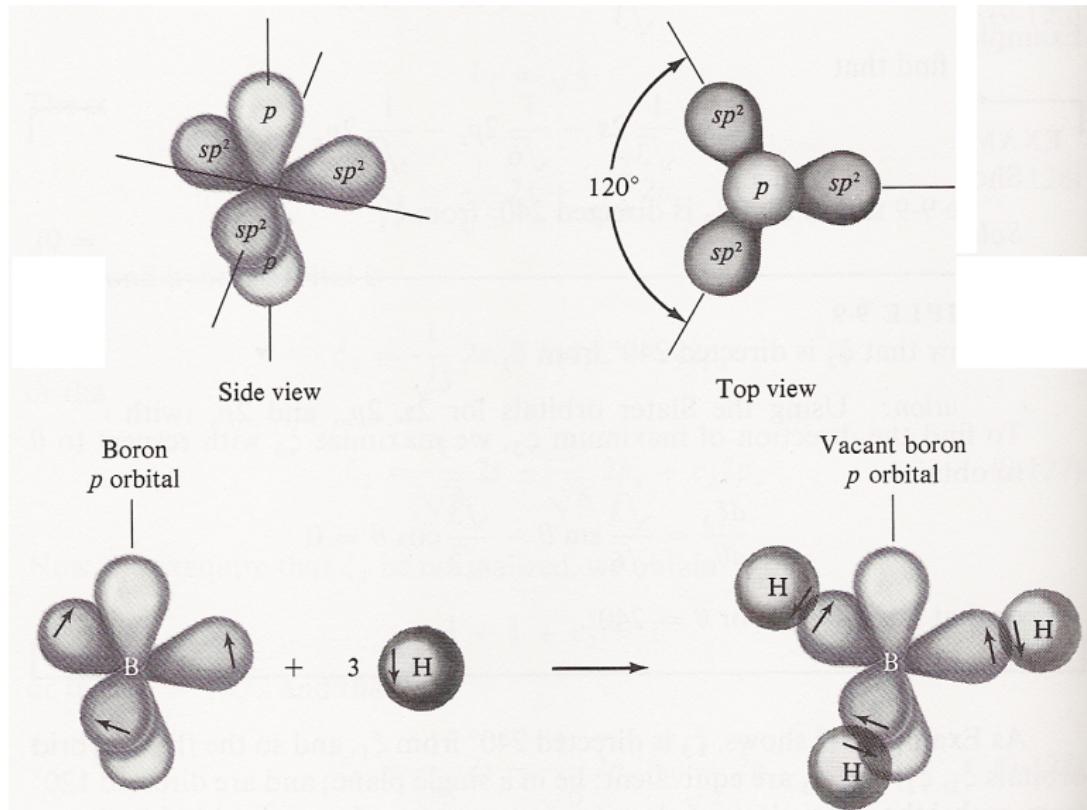
$$\xi_3 = a_3 2s + b_3 2p_z + c_3 2p_x$$

and

$$\psi_{2p_x} = \left( \frac{3}{4\pi} \right)^{1/2} R(r) \sin \theta \cos \phi$$

Using normalization and orthogonalization arguments you can verify the position of these three orbitals on your own.

# Hybrid Orbitals - sp<sup>2</sup>



# Hybrid Orbitals - sp<sup>3</sup>

Consider the molecule CH<sub>4</sub>. In this case, one 2s electron is promoted to the empty 2p orbital and four equivalent hybrid orbitals exist which point to the vertices of a regular tetrahedron. The hybrid orbitals on the carbon atom are

$$\xi_1 = a_1 2s_C + b_1 2p_{xC} + c_1 2p_{yC} + d_1 2p_{zC}$$

$$\xi_2 = a_2 2s_C + b_2 2p_{xC} + c_2 2p_{yC} + d_2 2p_{zC}$$

$$\xi_3 = a_3 2s_C + b_3 2p_{xC} + c_3 2p_{yC} + d_3 2p_{zC}$$

$$\xi_4 = a_4 2s_C + b_4 2p_{xC} + c_4 2p_{yC} + d_4 2p_{zC}$$

The molecular bond orbitals can be expressed as

$$\psi_1 = u_1 1s_A + v_1 \xi_1$$

$$\psi_2 = u_2 1s_B + v_2 \xi_2$$

$$\psi_3 = u_3 1s_C + v_3 \xi_3$$

$$\psi_4 = u_4 1s_D + v_4 \xi_4$$

# Hybrid Orbitals - sp<sup>3</sup>

By requiring the four hybrid orbitals to be equivalent, using the condition

$$a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$$

then

$$a_1 = a_2 = a_3 = a_4 = \frac{1}{\sqrt{4}}$$

Also, orient  $\xi_1$  to be along the z-axis so that  $b_1 = c_1 = 0$  and normalize which determines  $d_1 = \sqrt{3/4}$ . This means

$$\xi_1 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{3}{4}}2p_z$$

# Hybrid Orbitals - sp<sup>3</sup>

The second orbital,  $\xi_2$ , can lie in the x-z plane which means that  $c_2 = 0$ . Requiring that

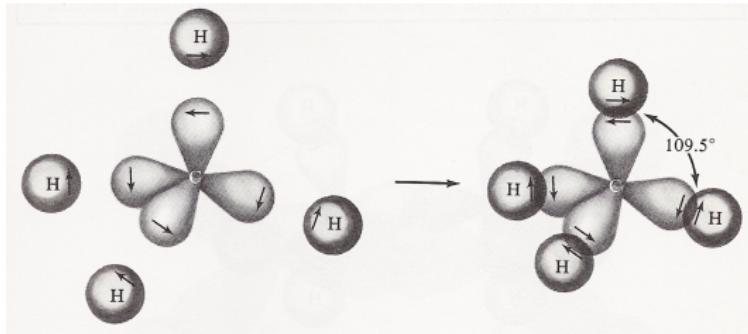
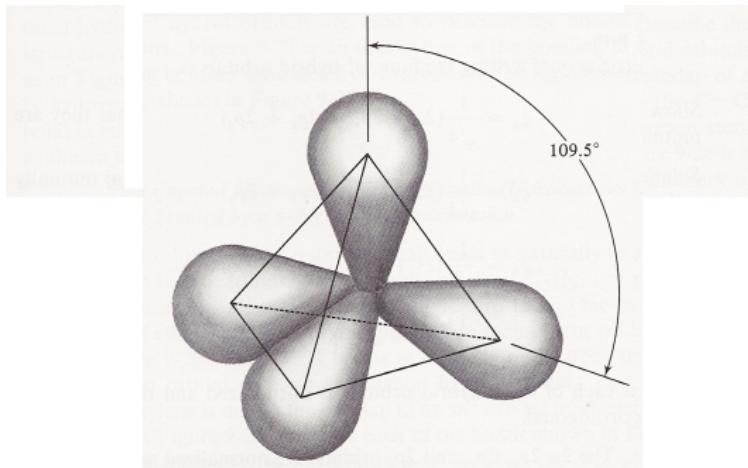
- $\xi_1$  and  $\xi_2$  are orthogonal -  $d_2 = -1/\sqrt{12}$
- $\xi_2$  is normalized -  $b_2 = \sqrt{2/3}$

which means that

$$\xi_2 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{2}{3}}2p_x - \frac{1}{\sqrt{12}}2p_z$$

Setting  $\phi = 0$  (maximizes the  $p_x$  orbital) and taking the derivative of  $\xi_2$  with respect to  $\theta$ , the position of its maximum is 109°.

# Hybrid Orbitals - sp<sup>3</sup>



# Summary

- Hybridized orbitals can be used to determine the geometry of molecules
  - Constructed from a linear combination of atomic orbitals