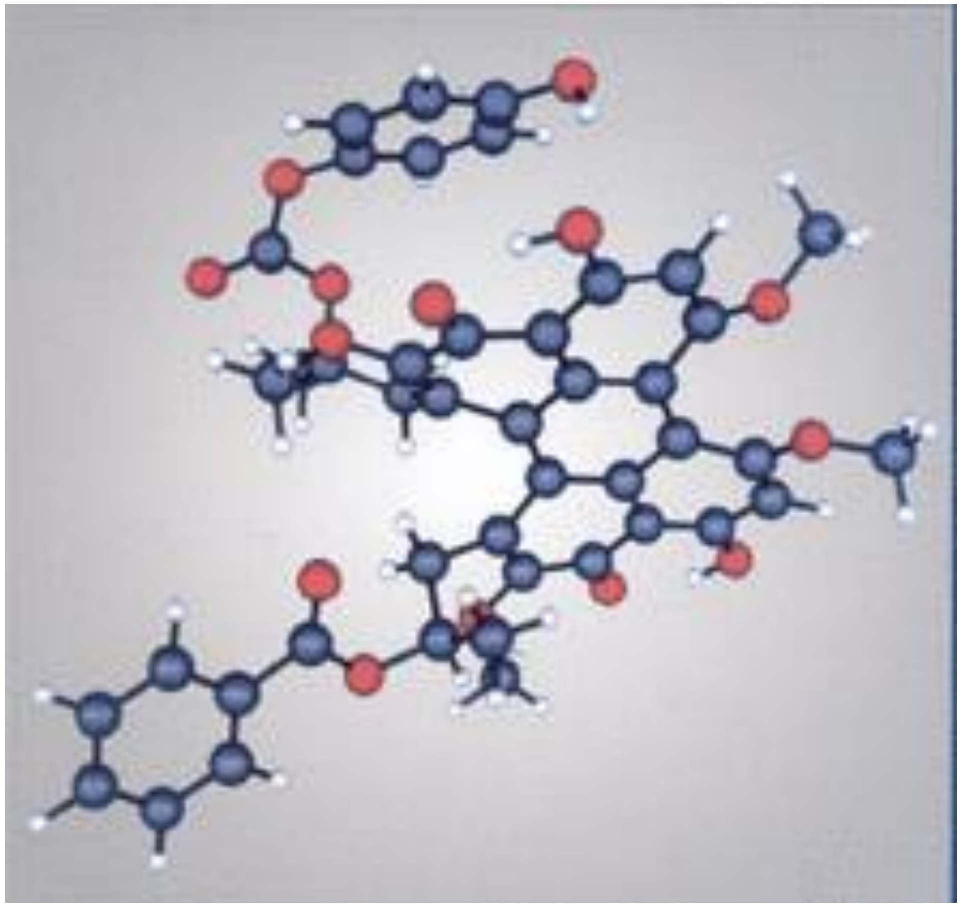
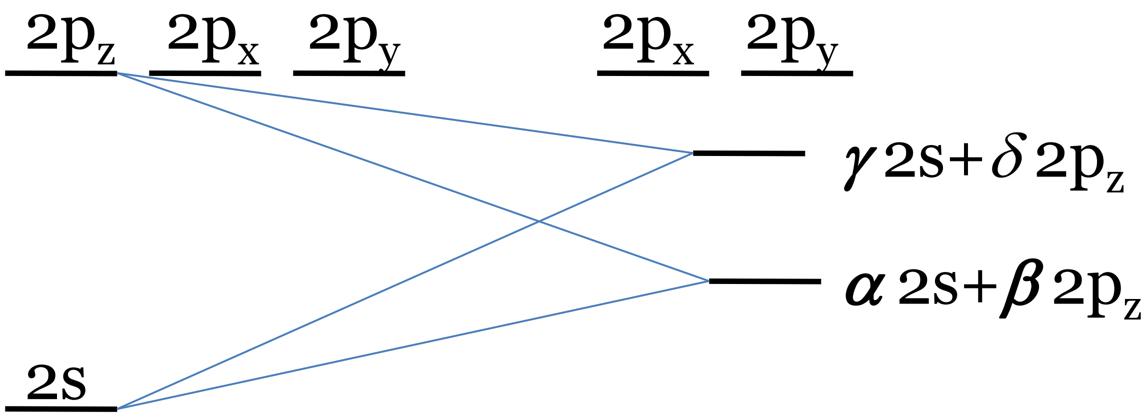
Lecture 10. Beyond Homonuclear Diatomics



Hybridization

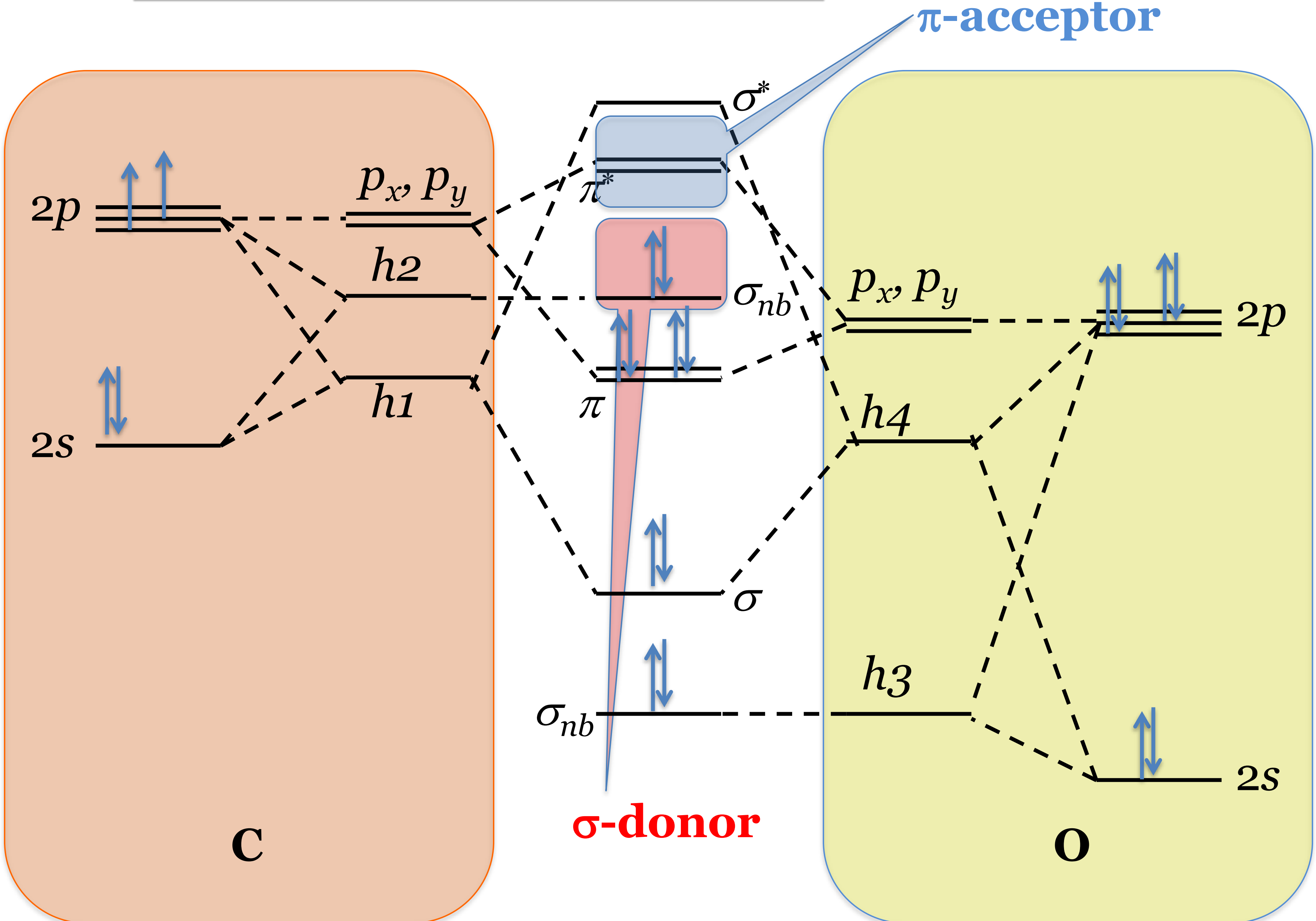
Linear combination of atomic orbitals **within an atom** leading to more effective bonding



- The ***coefficients*** α, β, γ and δ depend on ***field strength***
- ***Square*** of a coefficient = ***contribution*** of that AO in the hybrid orbital
- ***Equivalent*** hybrid orbitals (same *s*-contribution, same *p*-contribution in each hybrid orbital) have *same energies*
- Hybrid orbitals are ***ortho-normal*** to each other

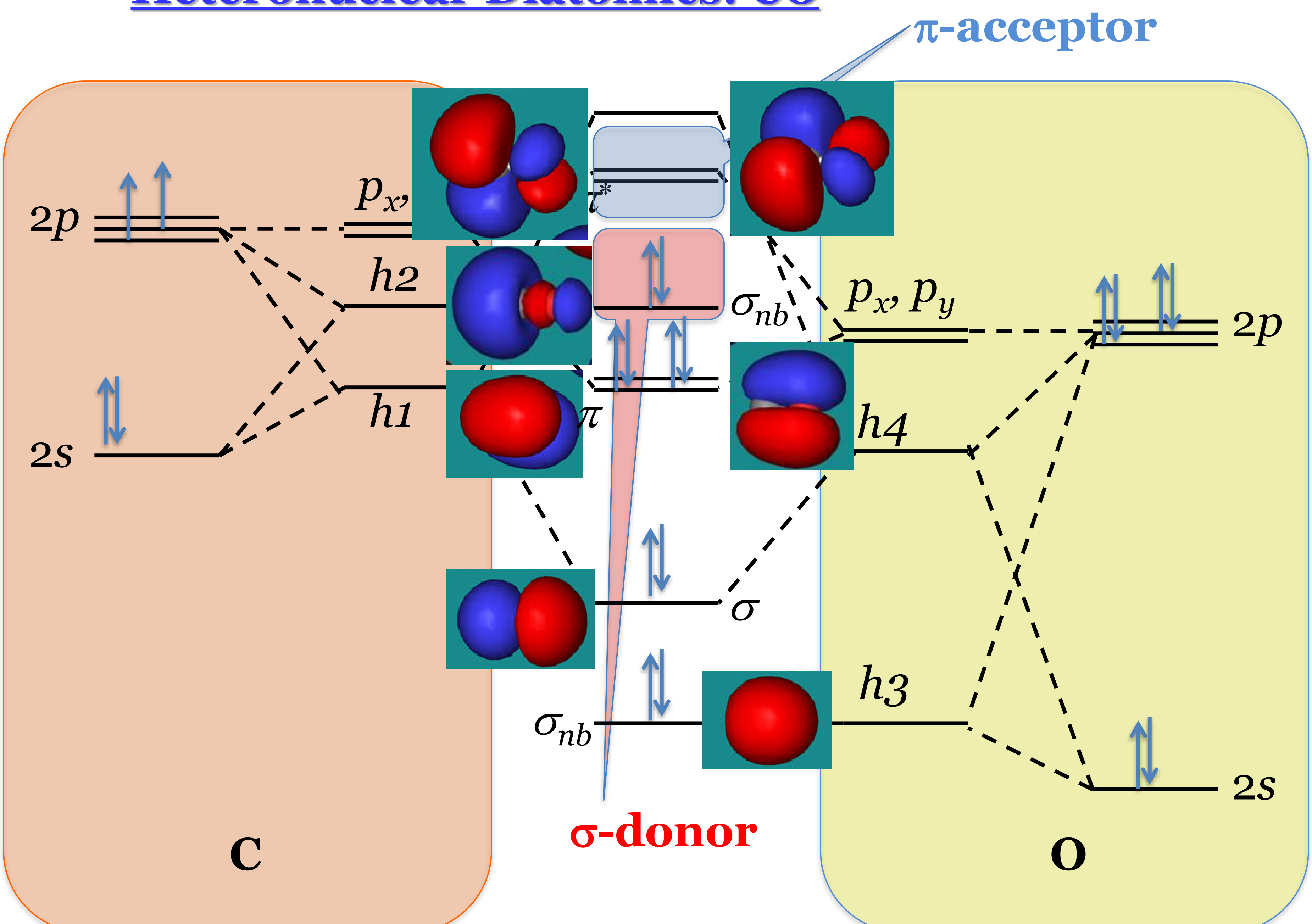
Hybridization origintes in VBT and relies on experimental results

Heteronuclear Diatomics: CO

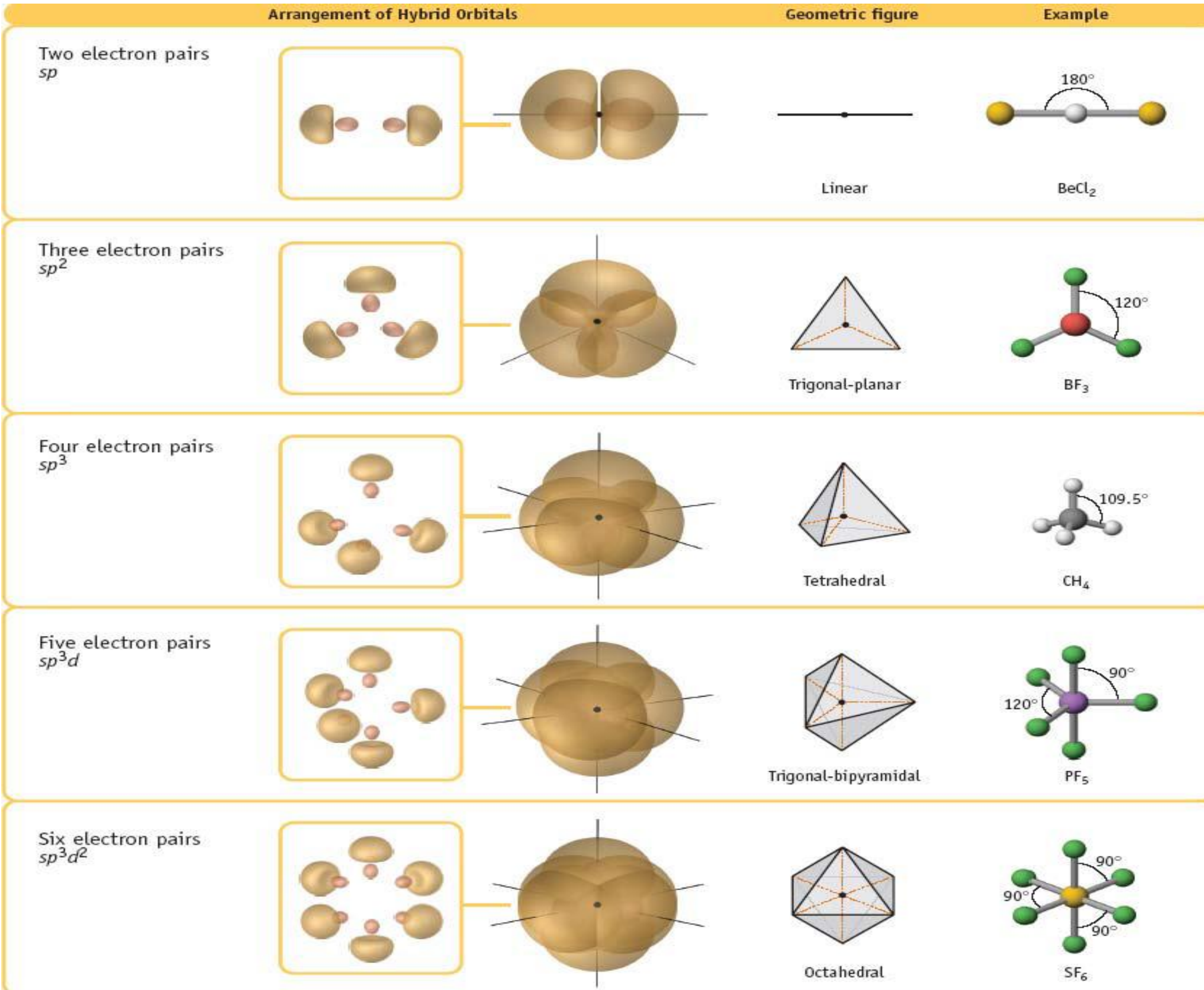


http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

Heteronuclear Diatomics: CO



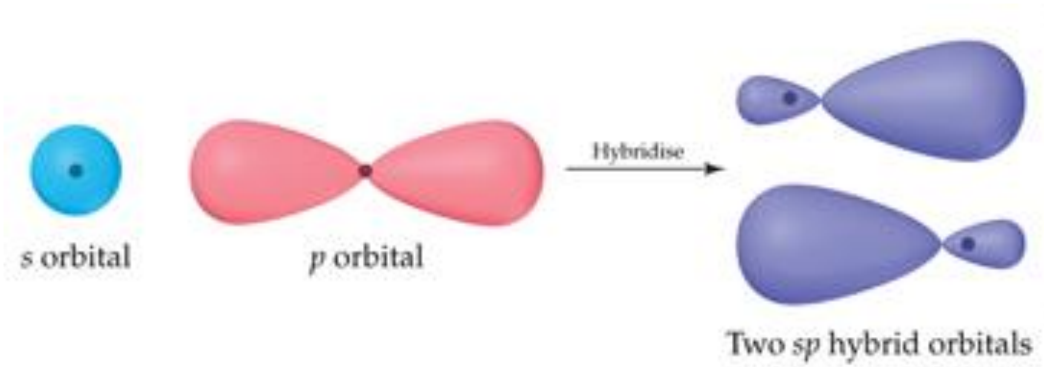
Polyatomic molecules: Geometry



s+p (sp) hybridization

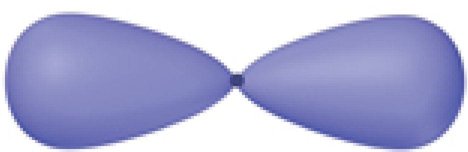
s and *p* orbital of the **SAME** atom!
No question of ***S*** (overlap integral)

2 equivalent hybrid orbitals of the same energy and shape (directions different)



$$\psi_2 = \frac{1}{\sqrt{2}}\left[\psi_s + \psi_p\right]$$

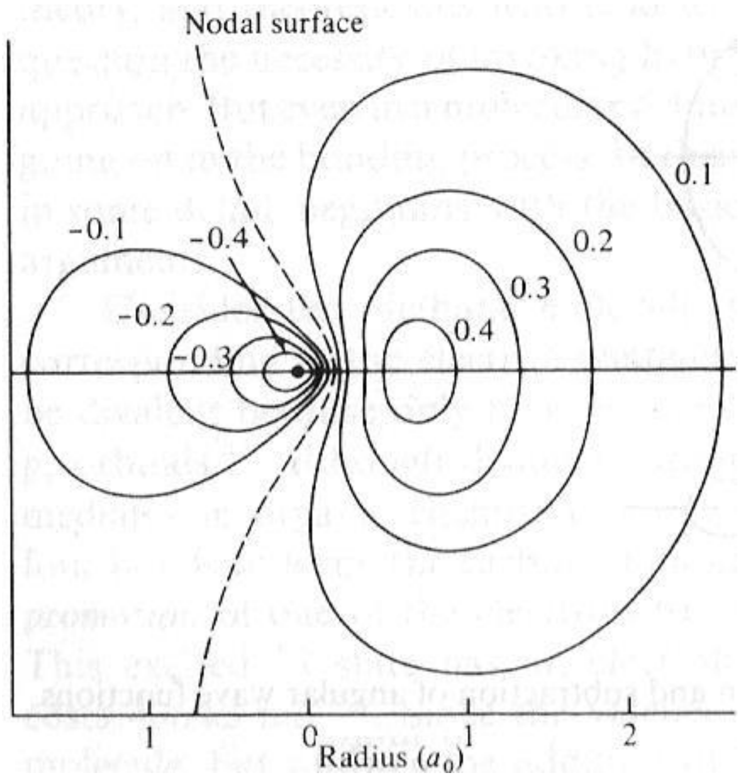
$$\psi_1 = \frac{1}{\sqrt{2}}\left[\psi_s - \psi_p\right]$$

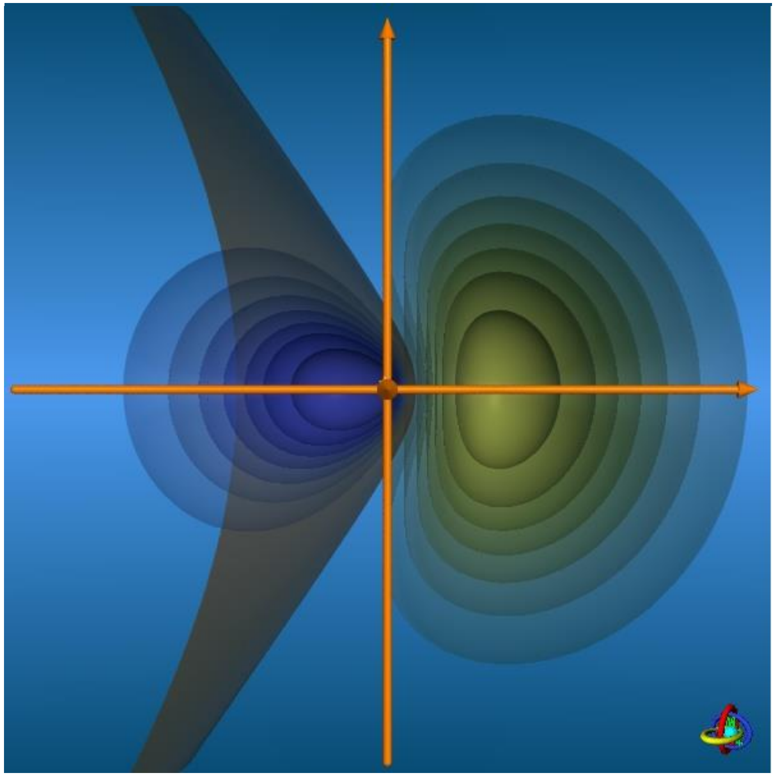


Linear geometry with
Hybridized atom at the center

Contribution from ***s*** = 0.5; contribution from ***p*** = 0.5

Contours of a *sp* hybrid orbital





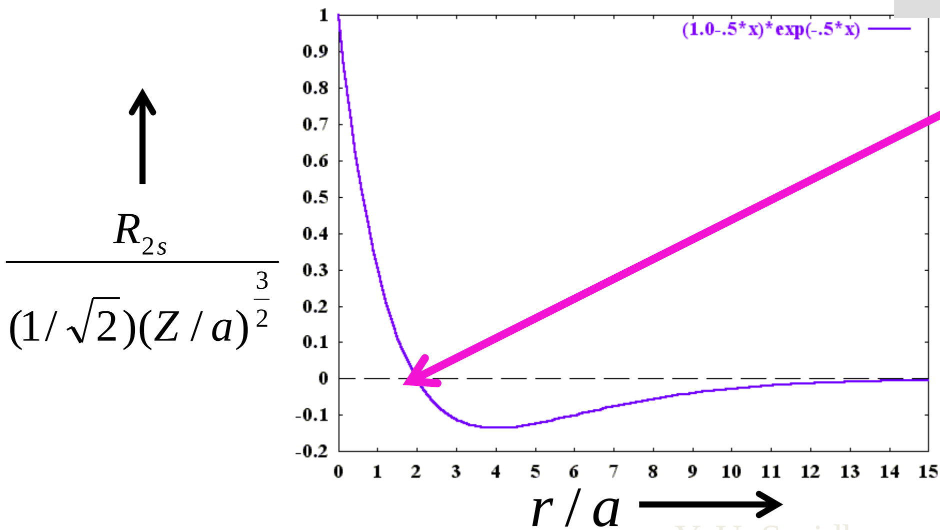
http://csi.chemie.tu-darmstadt.de/ak/immel/script/redirect.cgi?filename=http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/

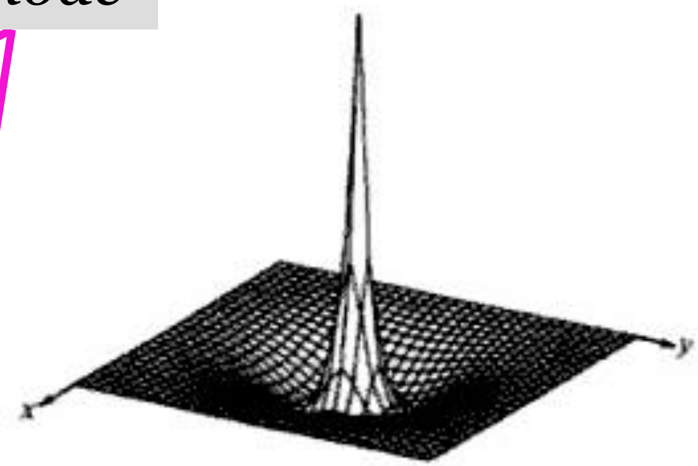
2s orbital

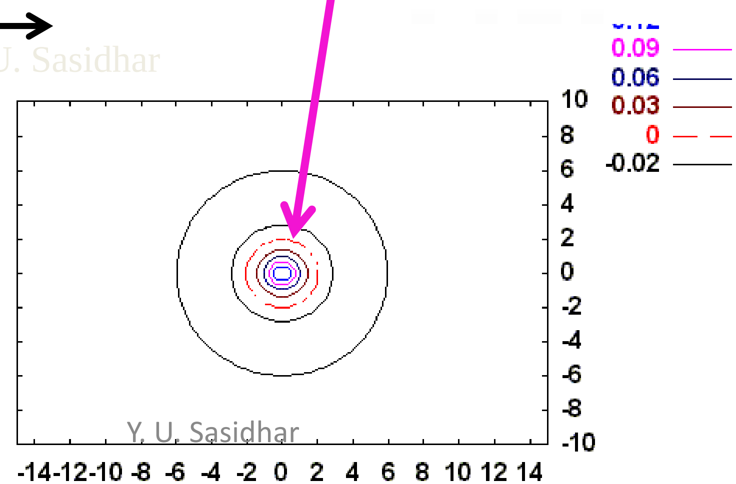
$$r = \frac{2a}{Z}$$

$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^0\left(2 - \frac{Zr}{a}\right)\exp(-Zr/2a)$$

radial node







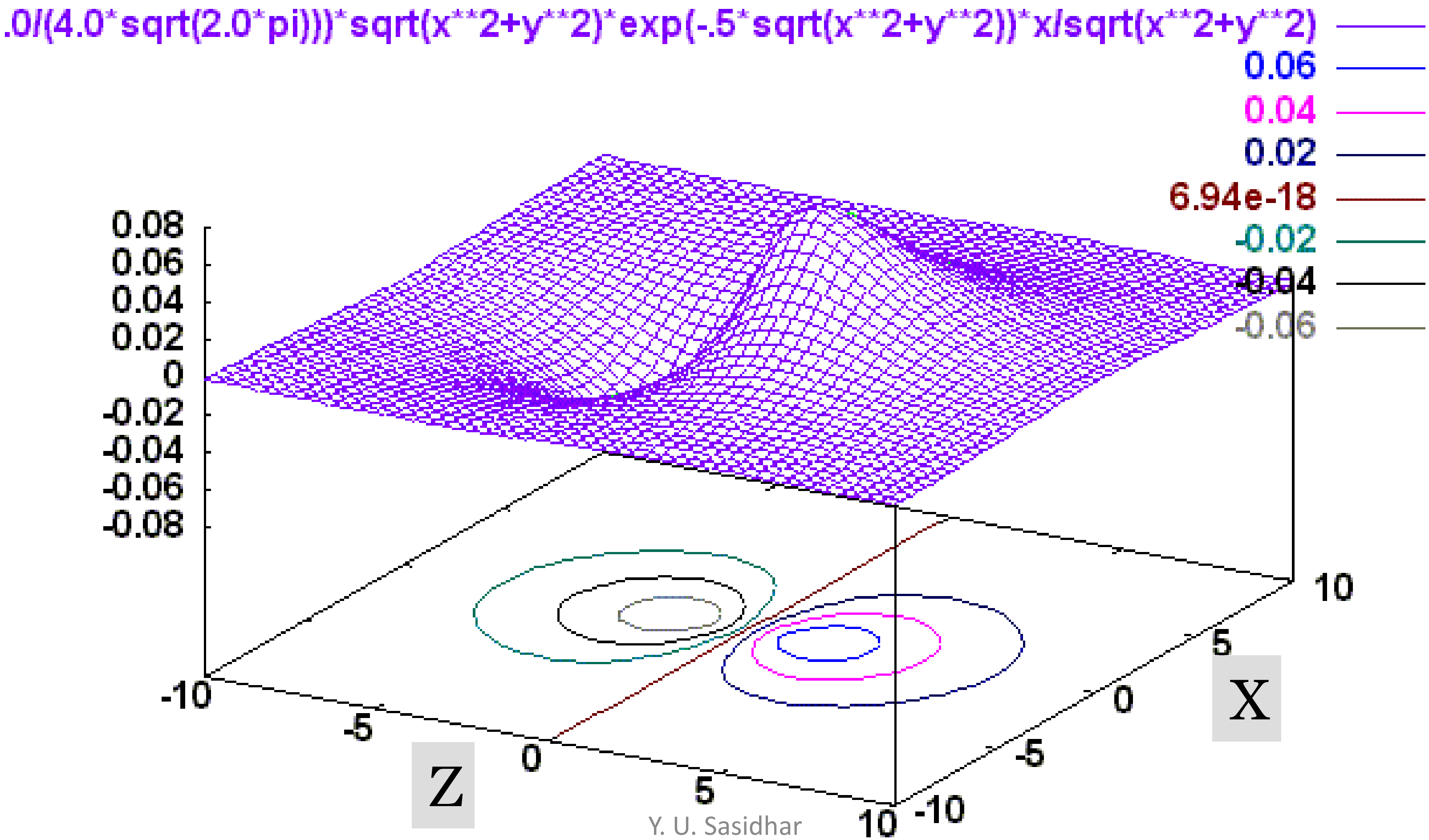
$2p_z$ orbital

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r^1 \exp(-Zr/2a)\cos\theta$$

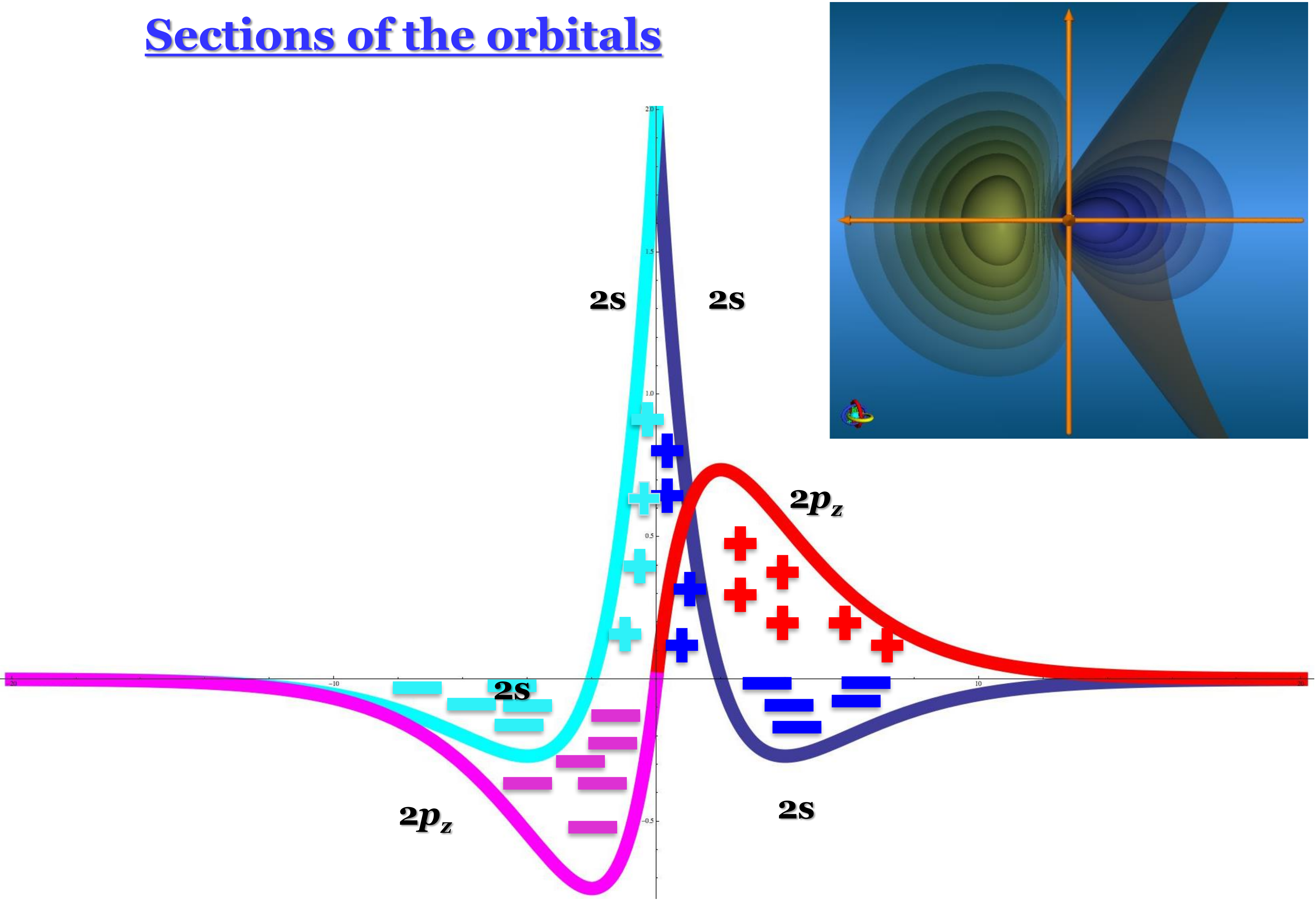
(2,1,0)

Angular Part

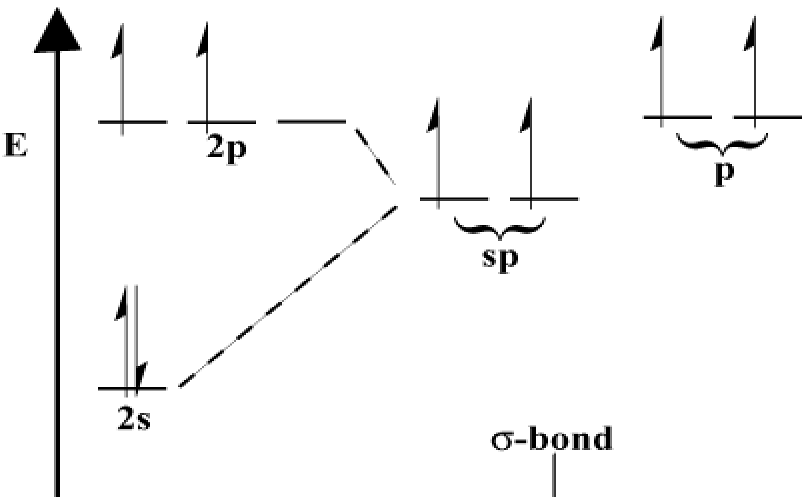
$\cos\theta = z/r$

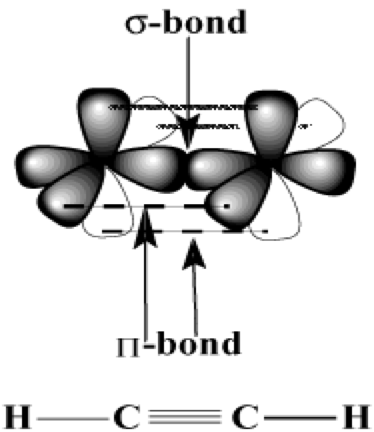


Sections of the orbitals

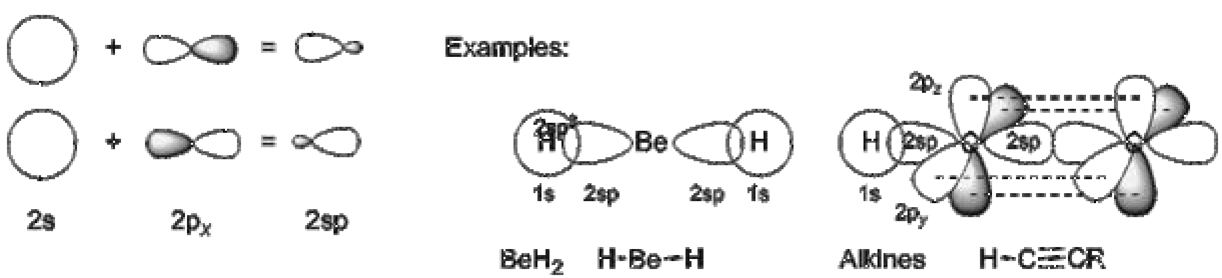


Bonding using *sp* hybrid orbitals



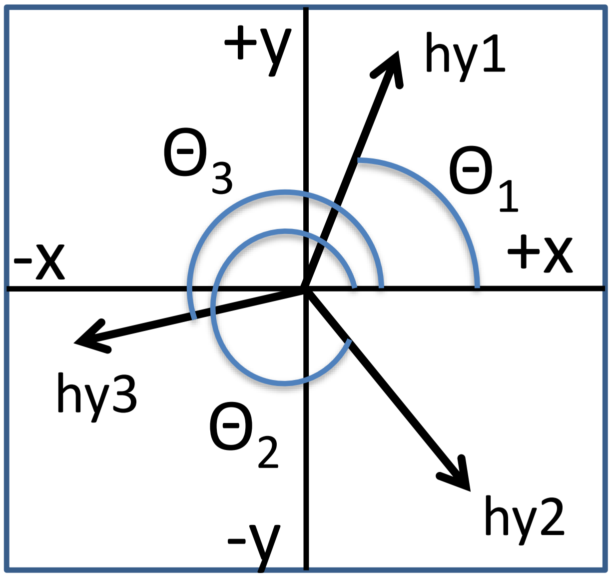


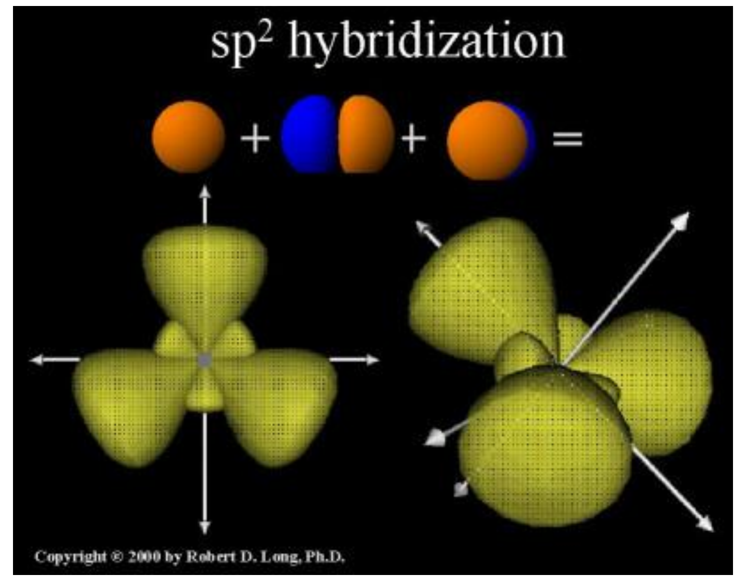
The other *p* orbitals are available for π bonding



Trigonal geometry: Mixing *s* & two *p* orbitals

p**$_x$* and ***p**$_y$* can be combined with ***s to get three 3 equivalent hybrids at 120° to each other



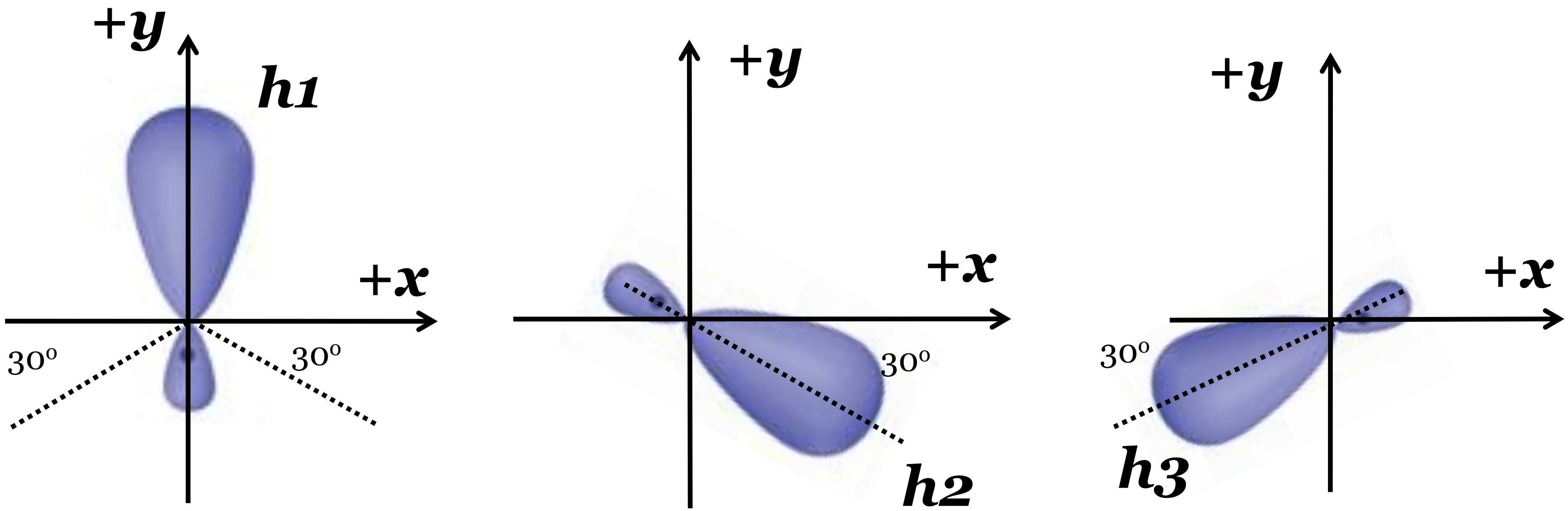


$$\varphi_{hy1} \equiv c_1\psi_s + \cos\theta_1.\psi_{p_x} + \sin\theta_1.\psi_{p_y}$$

$$\varphi_{hy2} \equiv c_1\psi_s + \cos\theta_2.\psi_{p_x} + \sin\theta_2.\psi_{p_y}$$

$$\varphi_{hy3} \equiv c_1\psi_s + \cos\theta_3.\psi_{p_x} + \sin\theta_3.\psi_{p_y}$$

Coefficients of AOs for specifically oriented *sp*² hybrid orbitals



$$\varphi_{h1}^{sp^2} = c_1\psi_s + c_2\psi_{p_x} + c_3\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_4\psi_s + c_5\psi_{p_x} + c_6\psi_{p_y}$$

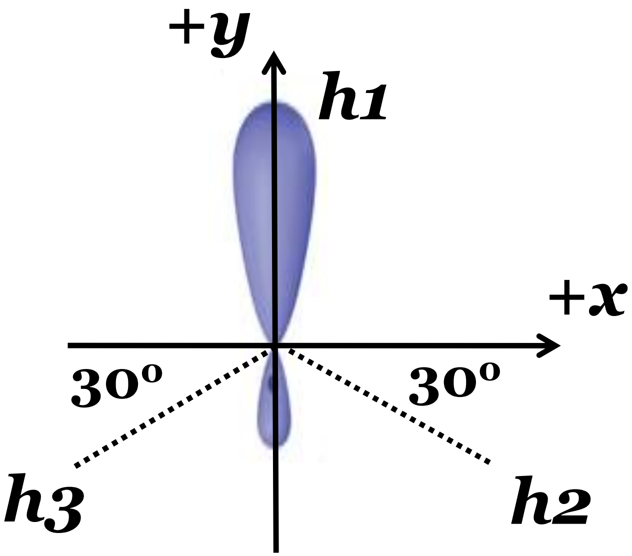
$$\varphi_{h2}^{sp^2} = c_7\psi_s + c_8\psi_{p_x} + c_9\psi_{p_y}$$

$$j_{h1}^{sp^2} = c_1 y_s + 0.y_{p_x} + c_3 y_{p_y}$$

$$j_{h2}^{sp^2} = c_4 y_s + c_5 y_{p_x} \boxed{-} c_6 y_{p_y}$$

$$j_{h3}^{sp^2} = c_7 y_s \boxed{-} c_8 y_{p_x} \boxed{-} c_9 y_{p_y}$$

Coefficients from the conditions of Orthonormality

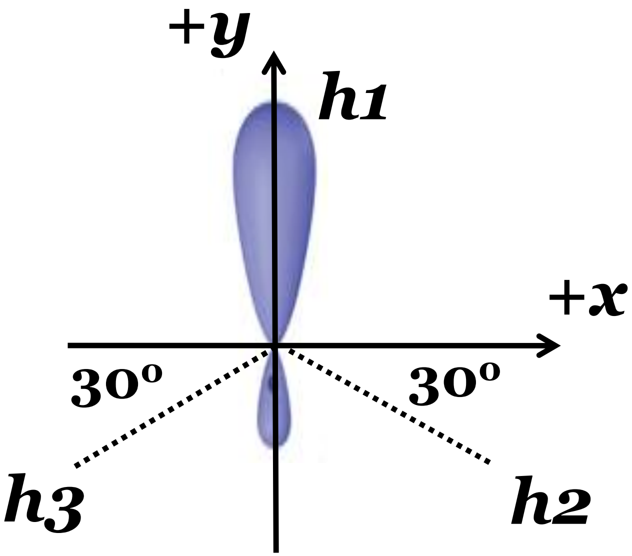


$$\varphi_{h1}^{sp^2} = c_1\psi_s + 0.\psi_{p_x} + c_3\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_4\psi_s + c_5\psi_{p_x} - c_6\psi_{p_y}$$

$$\varphi_{h3}^{sp^2} = c_7\psi_s - c_8\psi_{p_x} - c_9\psi_{p_y}$$

Coefficients from the conditions of Orthonormality



$$c_1^2 + c_4^2 + c_7^2 = 1 \ \text{(Total s-contribution)}$$

$$c_1 = c_4 = c_7 \ \text{(s contributes equally)}$$

$$c_2 = 0 \ (\mathrm{h}_1 \ \text{along y})$$

$$|c_5| = |c_8| (symmetry)$$

$$|c_6| = |c_9| (symmetry)$$

Each j is *normalized*

$$c_1^2 + 0 + c_3^2 = 1$$

$$c_1^2 + c_5^2 + c_6^2 = 1$$

p_x *and* p_y *Coeffs.*

$$0 + c_5^2 + c_5^2 = 1$$

$$c_3^2 + c_6^2 + c_6^2 = 1$$

j_i, j_j : *orthogonal*

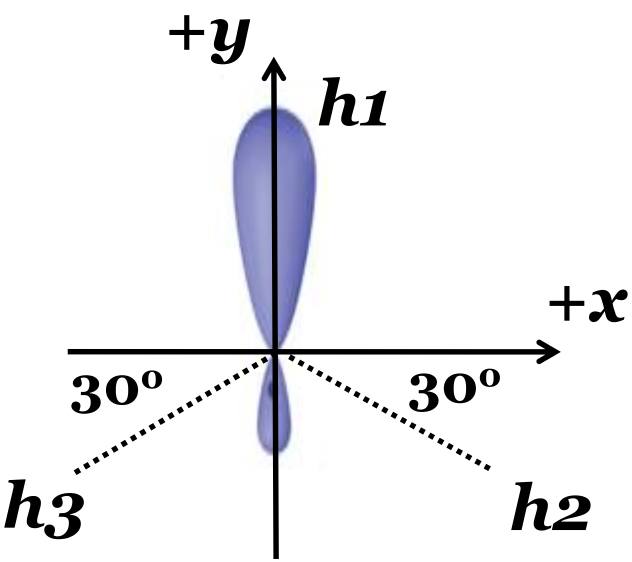
$$c_1 c_1 + 0 c_5 + c_3 c_6 = 0.....$$

$$j_{h1}^{sp^2} = c_1 y_s + 0.y_{p_x} + c_3 y_{p_y}$$

$$j_{h2}^{sp^2} = c_1 y_s + c_5 y_{p_x} \boxed{-} c_6 y_{p_y}$$

$$j_{h3}^{sp^2} = c_1 y_s \boxed{-} c_5 y_{p_x} \boxed{-} c_6 y_{p_y}$$

Signs and coefficients for these particular *sp*² hybrids



$$\varphi_{h1}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + 0.\psi_{p_x} + \sqrt{\frac{2}{3}}\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

$$\varphi_{h3}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

Square of coefficients ➔ Contribution from s=0.33; from p=0.66