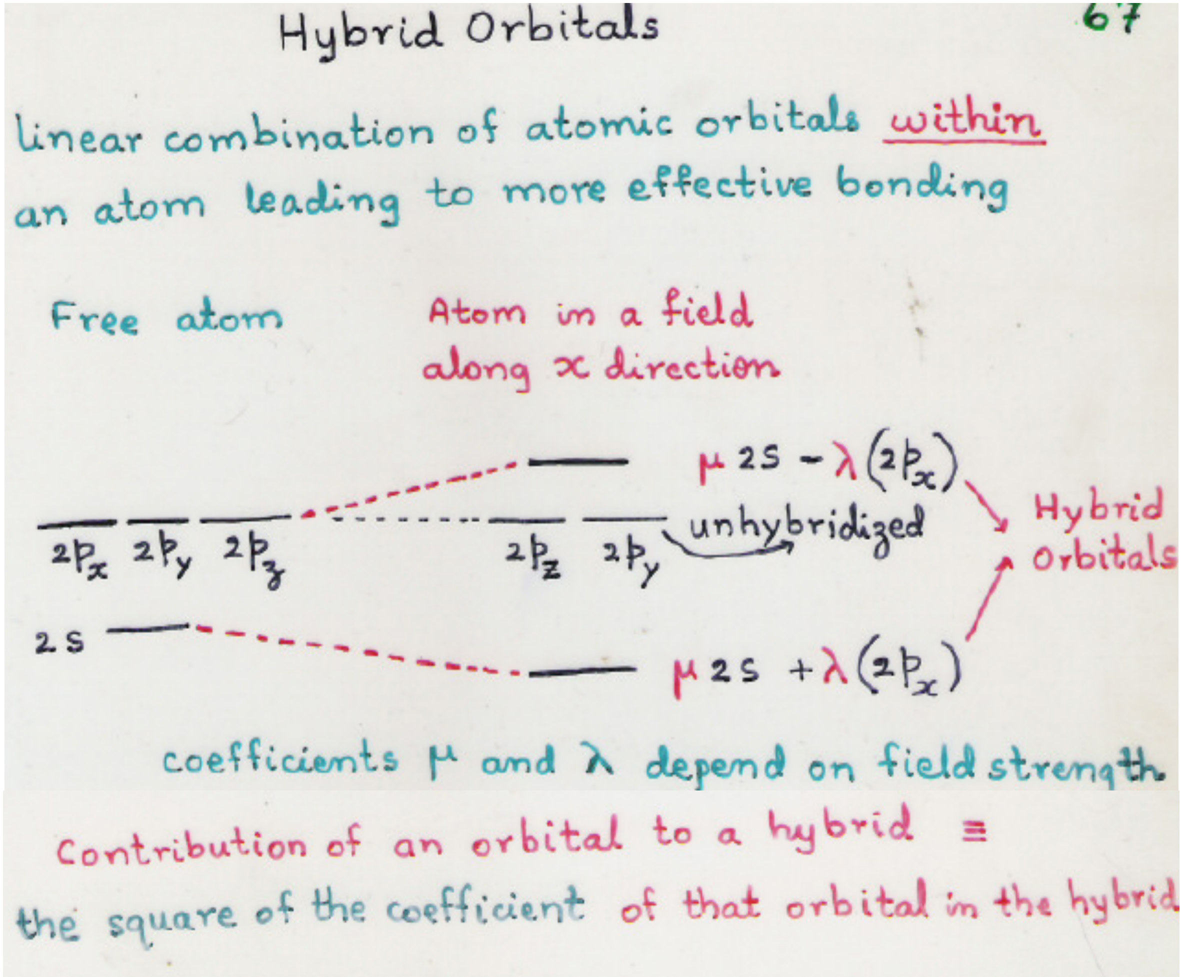
Hybrids: Linear Combination of S and P leads to lowering of energy

Linus Pauling, ~1930



- Hybridization is close to VBT. Use of experimental information
- All hybrid orbitals equivalent and are orthonormal to each other

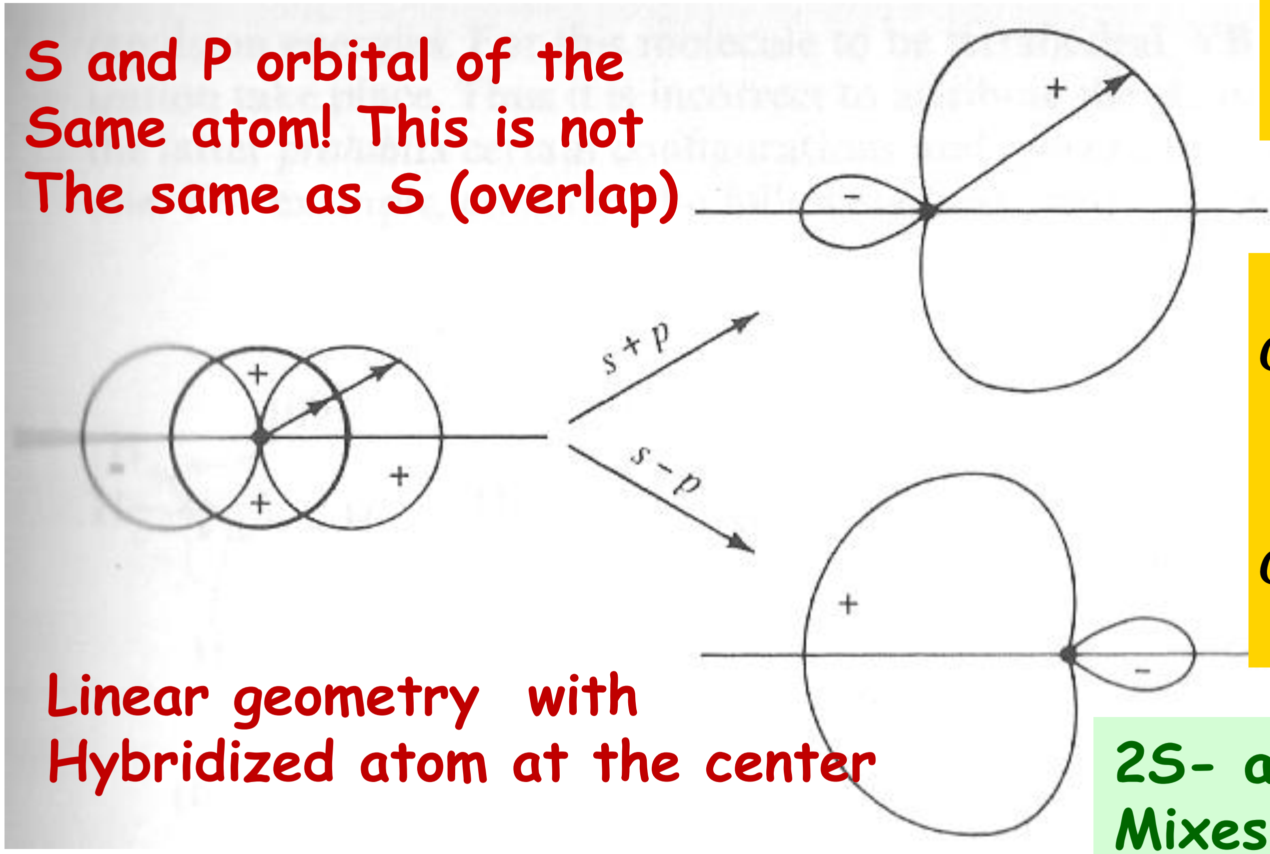
Linear Environment: s & 1-p mix: sp

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

$$\varphi_{h1}^{sp} = c_1\psi_s + c_2\psi_p$$

$$\varphi_{h2}^{sp} = c_1\psi_s - c_2\psi_p$$

S and P orbital of the Same atom! This is not The same as S (overlap)



$$\varphi_{h1}^{sp} = \frac{1}{\sqrt{2}}\psi_s + \frac{1}{\sqrt{2}}\psi_p$$

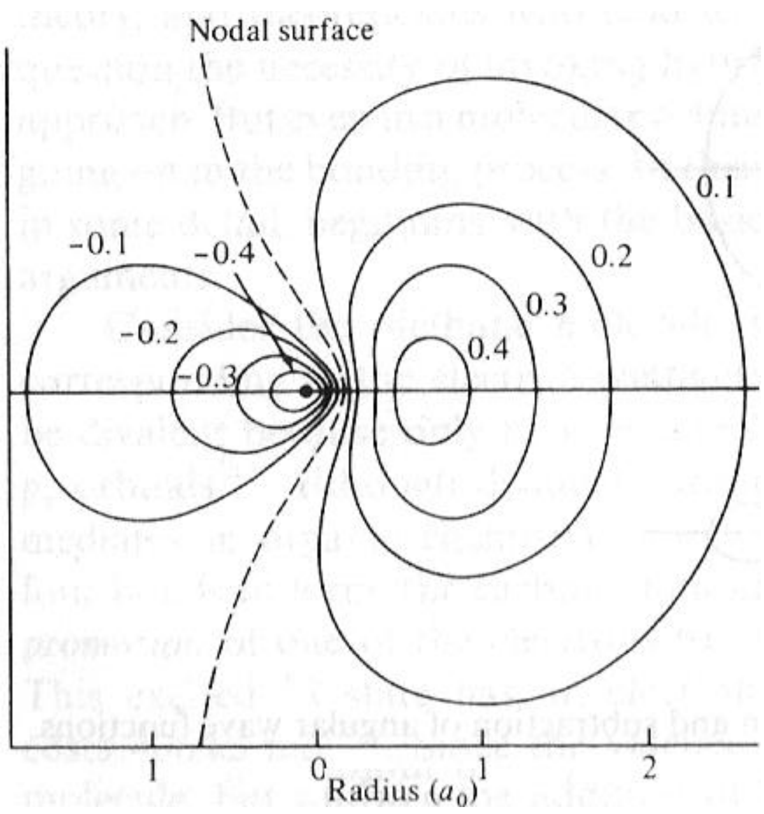
$$\varphi_{h2}^{sp} = \frac{1}{\sqrt{2}}\psi_s - \frac{1}{\sqrt{2}}\psi_p$$

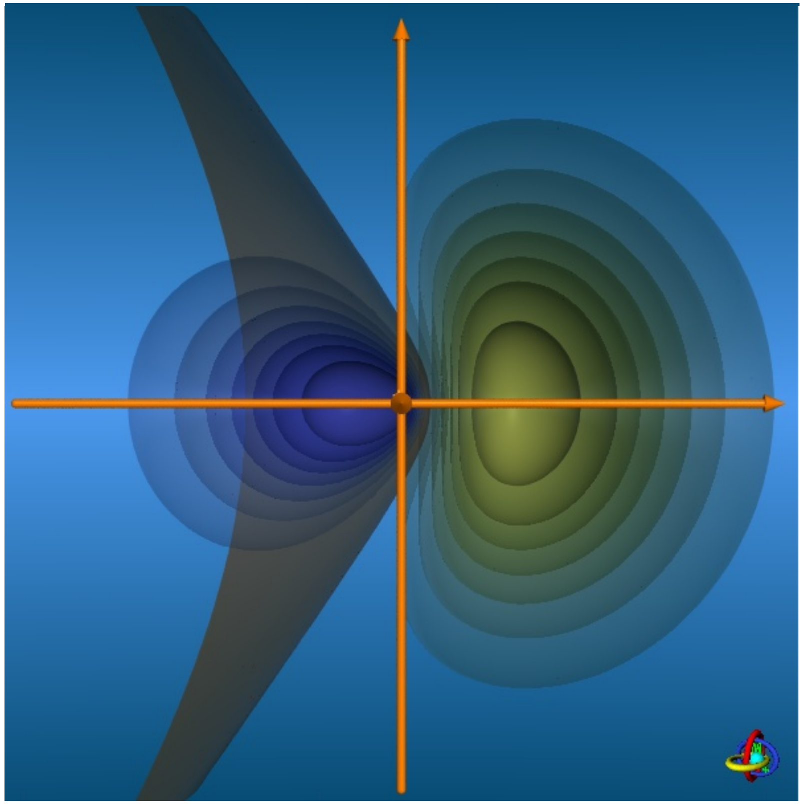
Linear geometry with Hybridized atom at the center

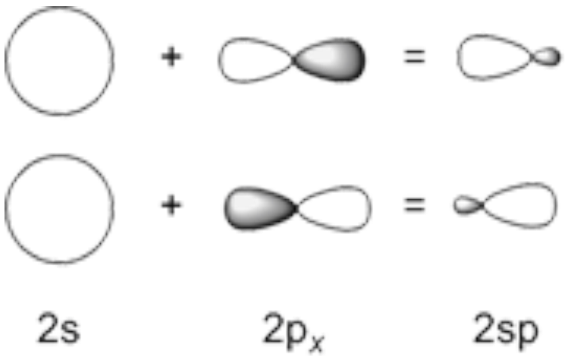
2S- and 2P- (similar energy) Mixes to form hybrid orbital which forms a MO with H (1S)

Contribution from s=0.5; contribution from p=0.5
Have to normalize each hybridized orbital

Contours & bonding of sp-hybridization

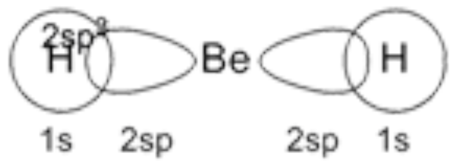




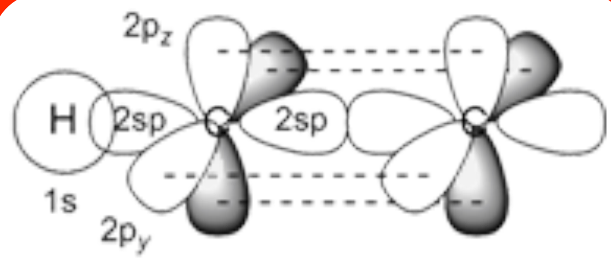


2 more p-orbital available for bonding

Examples:



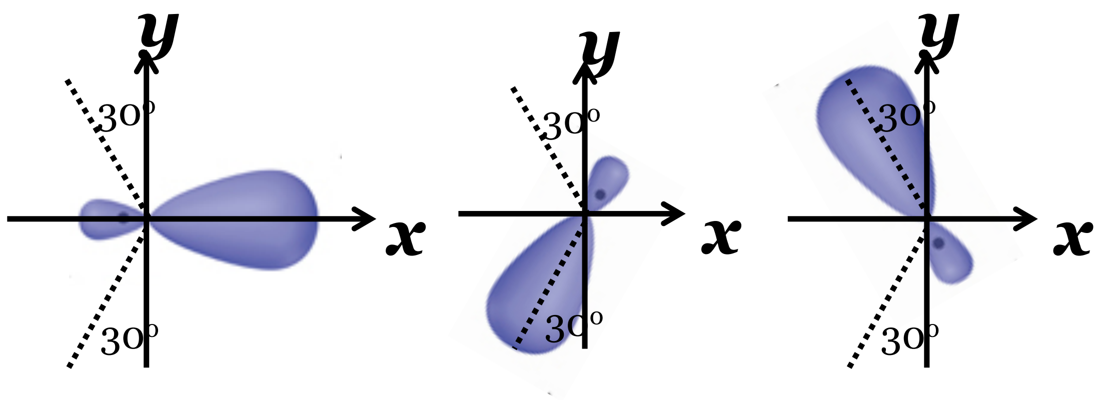
BeH_2 H-Be−H

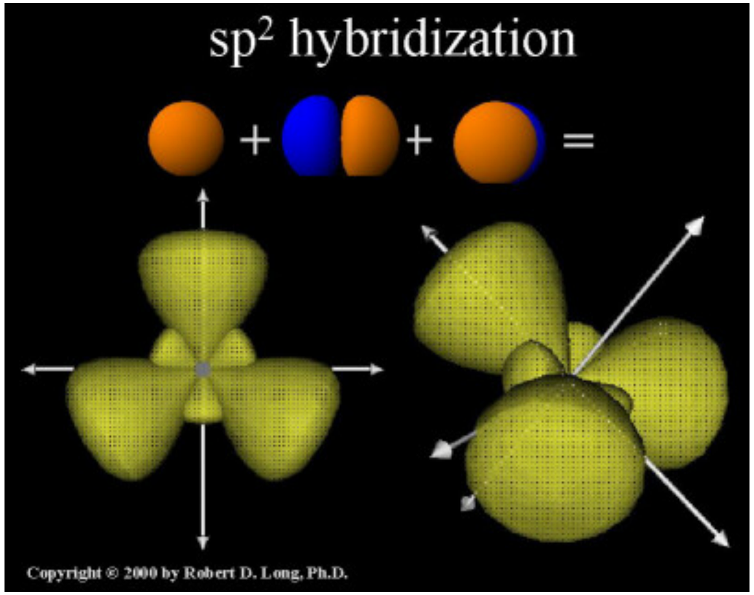


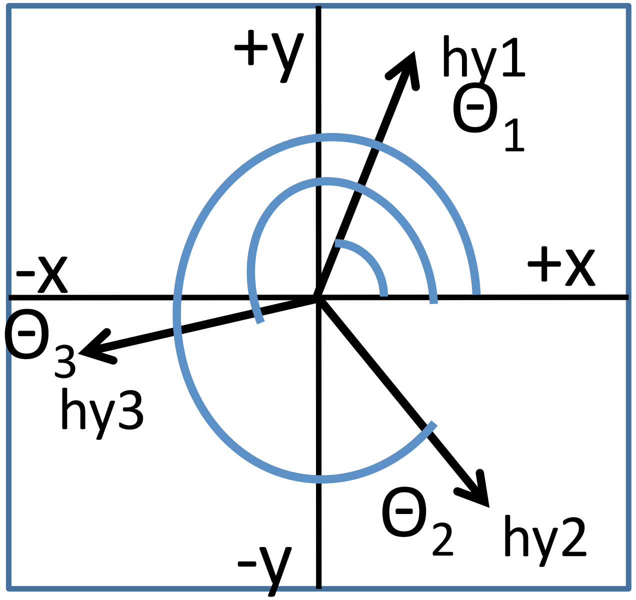
Alkines H−C≡CR

Trigonal Environment: Mixing s & 2-p

$\boldsymbol{p_x}$ and $\boldsymbol{p_y}$ can be combined with $\boldsymbol{s}$ to get three 3 equivalent hybrids at 120° to each other







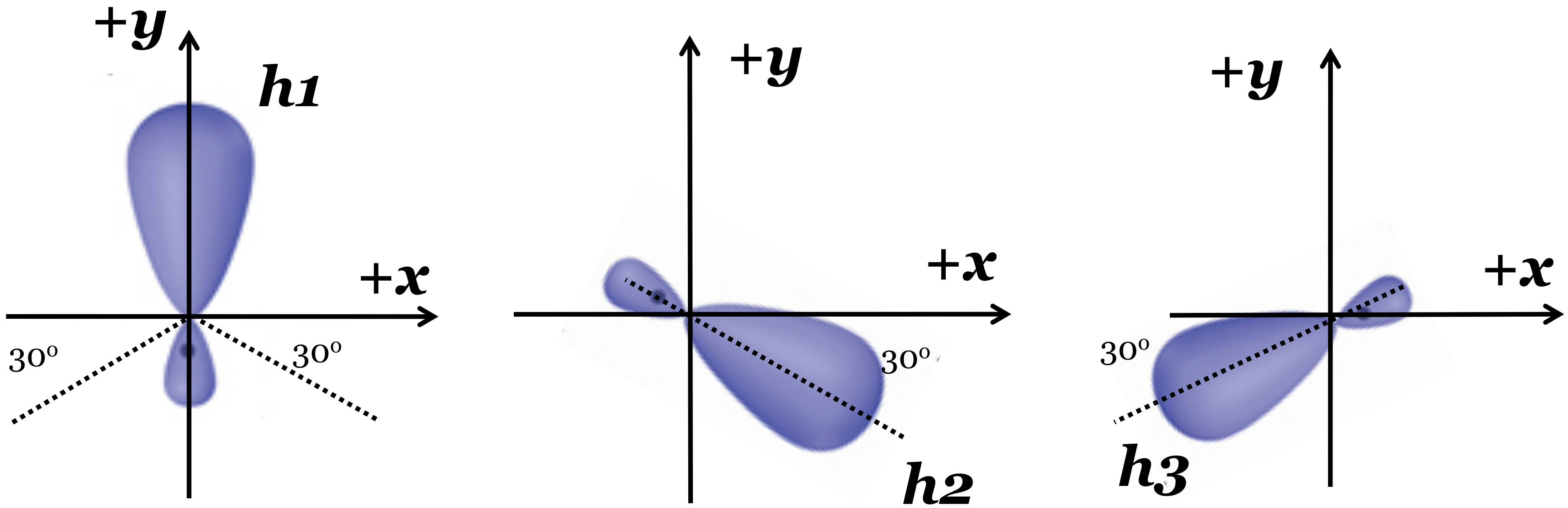
Signs of un-normalized hybrid orbitals

$$\varphi_{hy1} \equiv c_1\psi_s + Cos\theta_1.\psi_{p_x} + Sin\theta_1.\psi_{p_y}$$

$$\varphi_{hy2} \equiv c_1\psi_s + Cos\theta_2.\psi_{p_x} + Sin\theta_2.\psi_{p_y}$$

$$\varphi_{hy3} \equiv c_1\psi_s + Cos\theta_3.\psi_{p_x} + Sin\theta_3.\psi_{p_y}$$

Signs of AOs for specific Sp² hybrid orbitals (given an orientation)



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

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

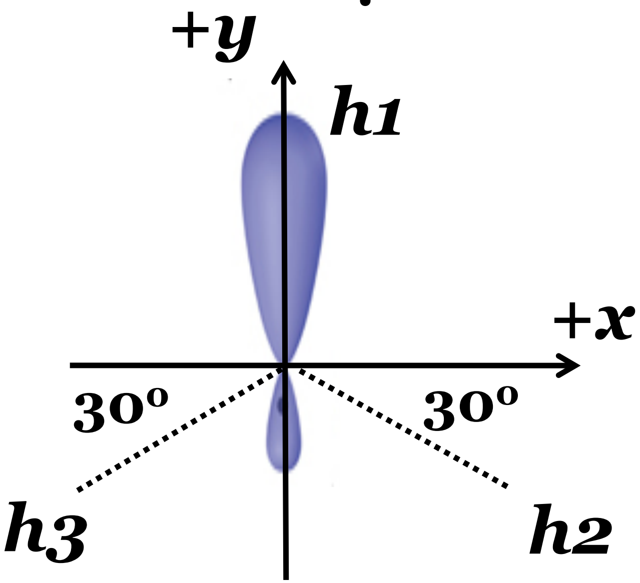
$$\varphi_{h2}^{sp^2} = c_7\psi_s + c_8\psi_{p_x} + c_9\psi_{p_y}$$

$$\varphi_{h1}^{sp^2} = c_1\psi_s + 0.c_2\psi_{p_x} + c_3\psi_{p_y}$$

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

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

How to obtain coefficients for this specific geometry of Sp²?



$$\varphi_{h1}^{sp^2} = c_1\psi_s + 0.c_2\psi_{p_x} + c_3\psi_{p_y}$$

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

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

$c_1^2 + c_4^2 + c_7^2 = 1$ (Total s-contribution)

$c_1 = c_4 = c_7$ (s contributes equally)

$c_2 = 0$ (h_1 along x)

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

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

φ_i, φ_j : *orthogonal*

$$c_1 c_4 + c_2 c_5 + c_3 c_6 = 0$$

$$c_4 c_7 + c_5 c_8 + c_6 c_9 = 0$$

$$c_7 c_1 + c_8 c_2 + c_9 c_3 = 0$$

Each φ is *normalized*

$$c_1^2 + c_2^2 + c_3^2 = 1$$

$$c_4^2 + c_5^2 + c_6^2 = 1$$

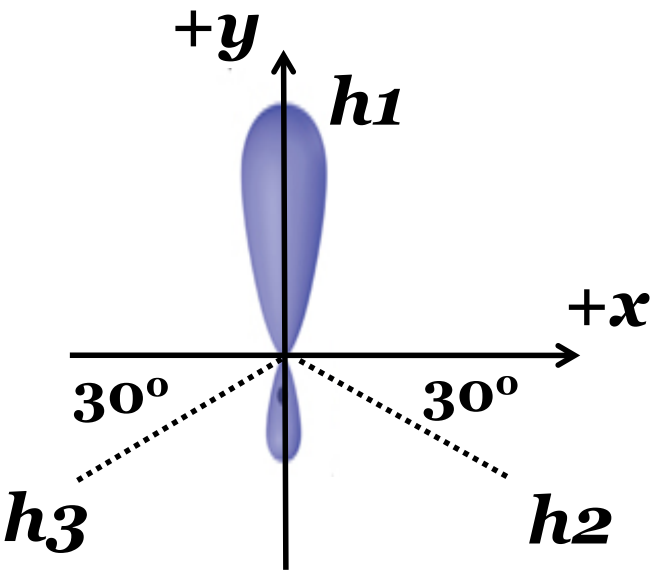
$$c_7^2 + c_8^2 + c_9^2 = 1$$

P_x *and* P_y *Coef f.s*

$$c_2^2 + c_5^2 + c_8^2 = 1$$

$$c_3^2 + c_6^2 + c_9^2 = 1$$

Signs and coefficients for these particular Sp² hybrids

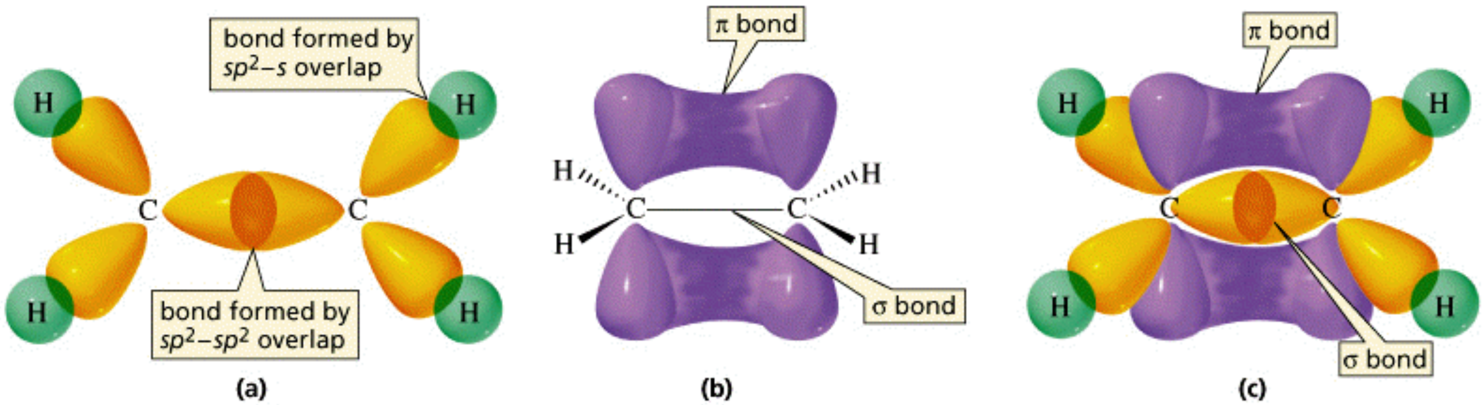


$$\varphi_{h1}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + 0.\psi_{p_x} + \sqrt{\frac{2}{3}}\psi_{p_y}$$

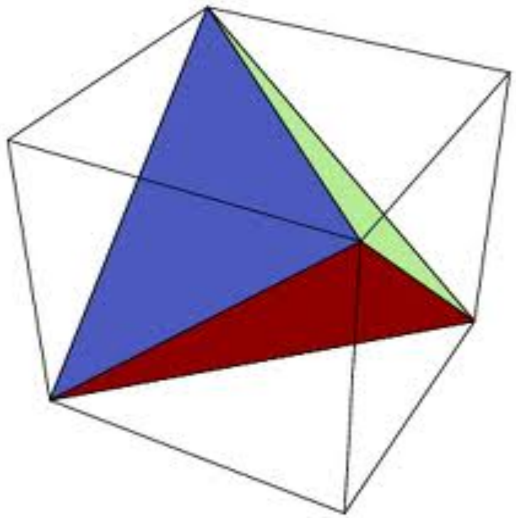
$$\varphi_{h2}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

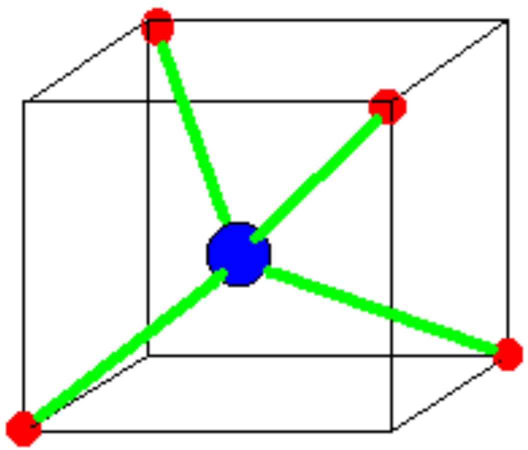
$$\varphi_{h3}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

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



Hybridization of s & 3-p:sp^3: Tetrahedral





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

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

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

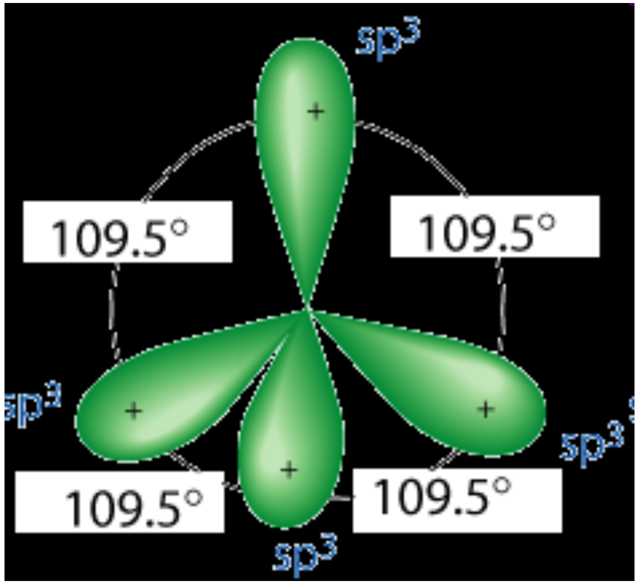
$$\varphi_{h4}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

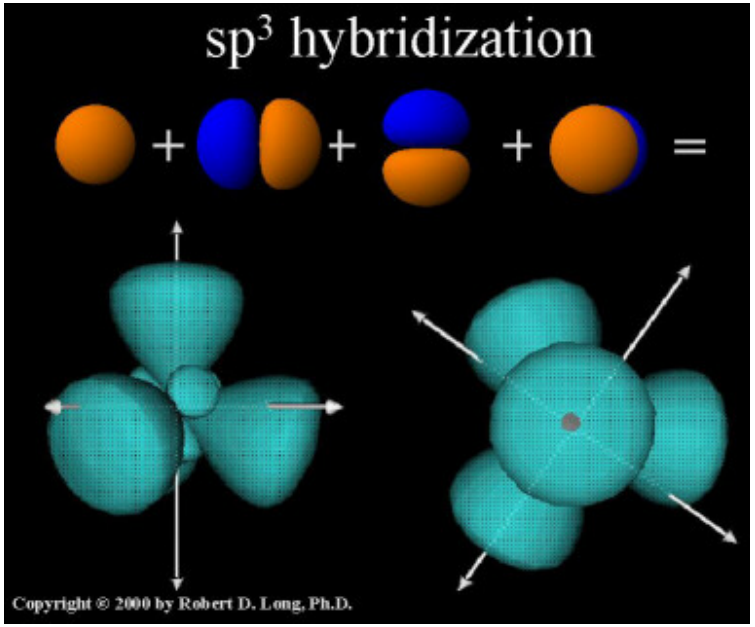
Contributions from s = 25%; p=75%

- **How do we calculate the coefficients?**

  Use orthonormality of hybrid-orbitals and symmetry arguments
- **There is no unique combination/solution (depends on the geometry!)**

What if h1 is oriented along z-axis?





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

$$\varphi_{h2} = \frac{1}{2}\psi_s - \sqrt{\frac{2}{3}}\psi_{p_x} + 0.\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

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

$$\varphi_{h4} = \frac{1}{2}\psi_s + \frac{1}{\sqrt{6}}\psi_{p_x} - \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

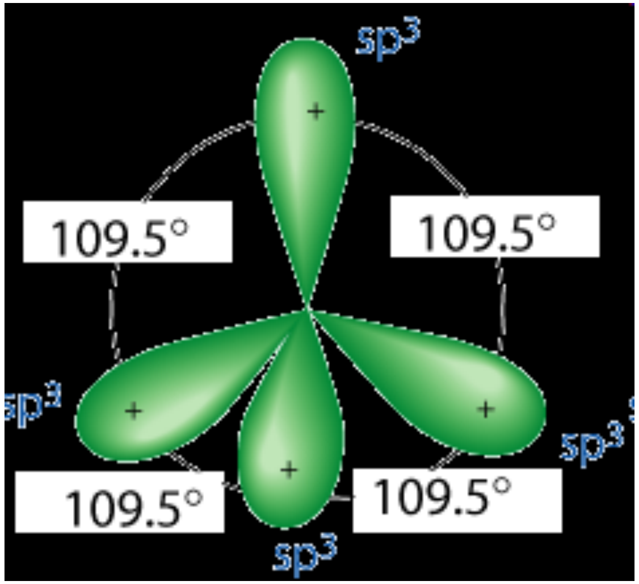
$$\varphi_{h1}^{sp^3} = c_1\psi_s + c_2\psi_{p_x} + c_3\psi_{p_y} + c_4\psi_{p_z}$$

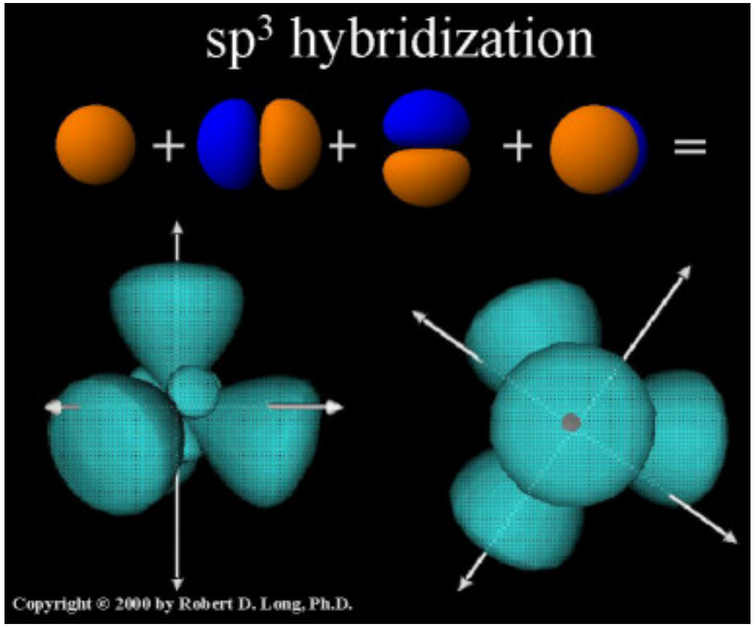
$$\varphi_{h2}^{sp^3} = c_1\psi_s + c_5\psi_{p_x} + c_7\psi_{p_y} + c_8\psi_{p_z}$$

$$\varphi_{h2}^{sp^3} = c_1\psi_s + c_9\psi_{p_x} + c_{10}\psi_{p_y} + c_{11}\psi_{p_z}$$

$$\varphi_{h4}^{sp^3} = c_1\psi_s + c_{12}\psi_{p_x} + c_{13}\psi_{p_y} + c_{14}\psi_{p_z}$$

What if h1 is oriented along z-axis?





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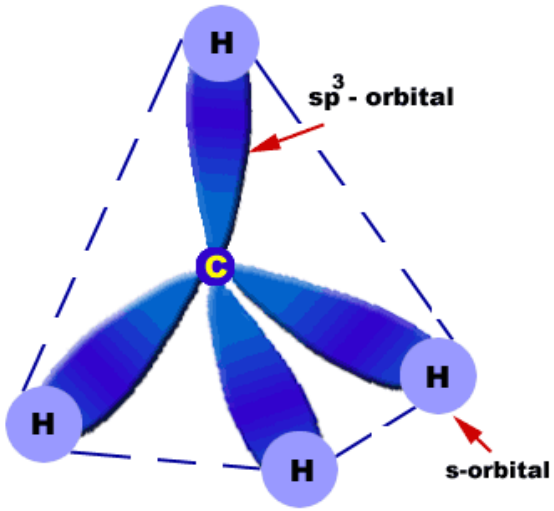
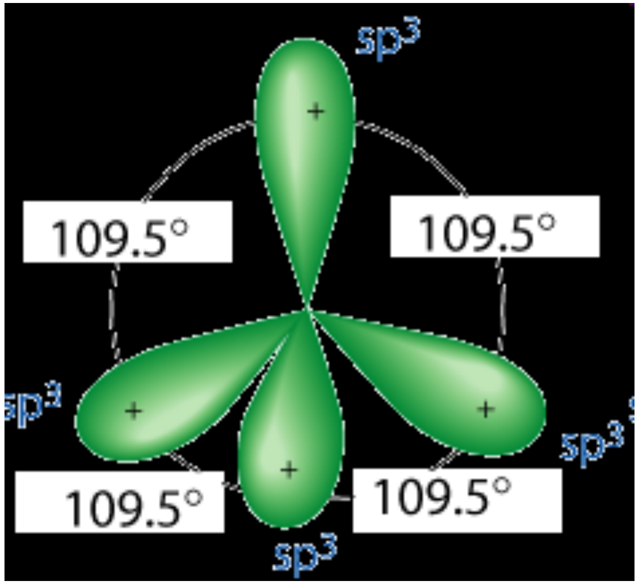
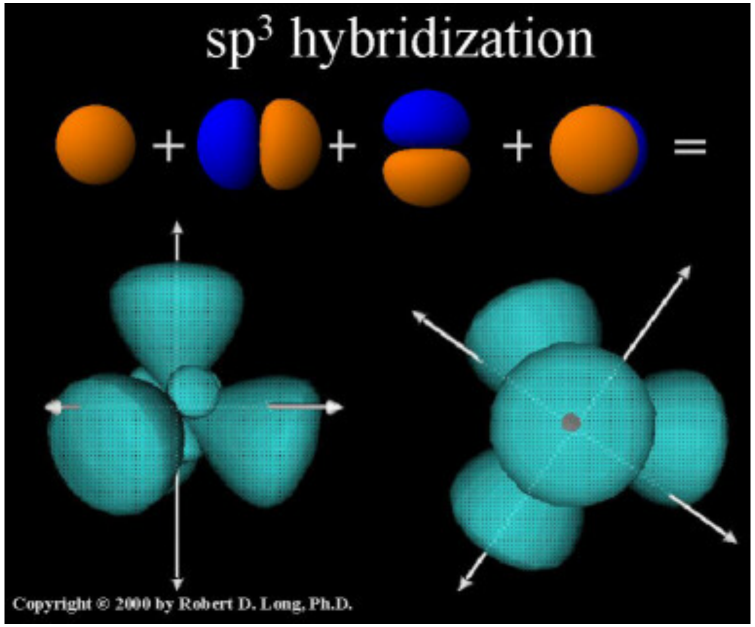


Orbital structure of methane

What if h1 is oriented along z-axis?





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

$$\varphi_{h2} = \frac{1}{2}\psi_s - \sqrt{\frac{2}{3}}\psi_{p_x} + 0.\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

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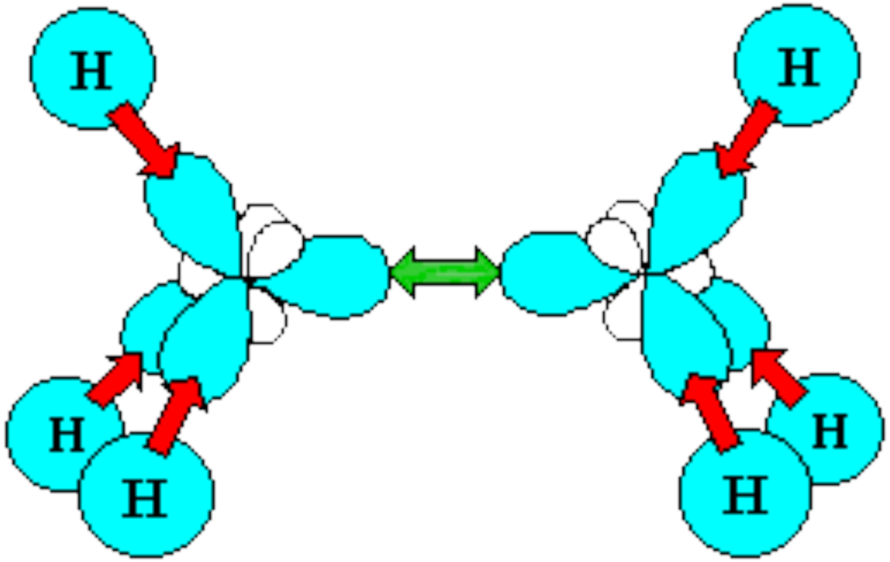
$$\varphi_{h4} = \frac{1}{2}\psi_s + \frac{1}{\sqrt{6}}\psi_{p_x} - \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$



Can we get back the angles from each pair of hybrid orbitals?

angle between two vectors

$$\vec{r_1}.\vec{r_2} = |r_1||r_2| Cos\theta$$

$$\theta = Cos^{-1}\left(\frac{\vec{r_1}.\vec{r_2}}{|r_1||r_2|}\right)$$

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

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

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

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

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

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$$\theta = Cos^{-1}\left(\frac{\vec{r_1}.\vec{r_2}}{|r_1||r_2|}\right)$$

$$\overrightarrow{\varphi_{h1}} \equiv + \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h2}} \equiv - \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h2}} \equiv + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h4}} \equiv - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h1}} \equiv 0.\psi_{p_x} + 0.\psi_{p_y} + \frac{\sqrt{3}}{2}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h2}} \equiv +\sqrt{\frac{2}{3}}\psi_{p_x} + 0.\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h3}} \equiv -\frac{1}{\sqrt{6}}\psi_{p_x} + \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h4}} \equiv -\frac{1}{\sqrt{6}}\psi_{p_x} - \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

How to get angle between hybrids?

$$\theta_{ij} = Cos^{-1}\left(\frac{\overrightarrow{h_i}.\overrightarrow{h_j}}{|h_i||h_j|}\right)$$

$$\overrightarrow{\varphi_{h2}} \equiv +\sqrt{\frac{2}{3}}\psi_{p_x} + 0.\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

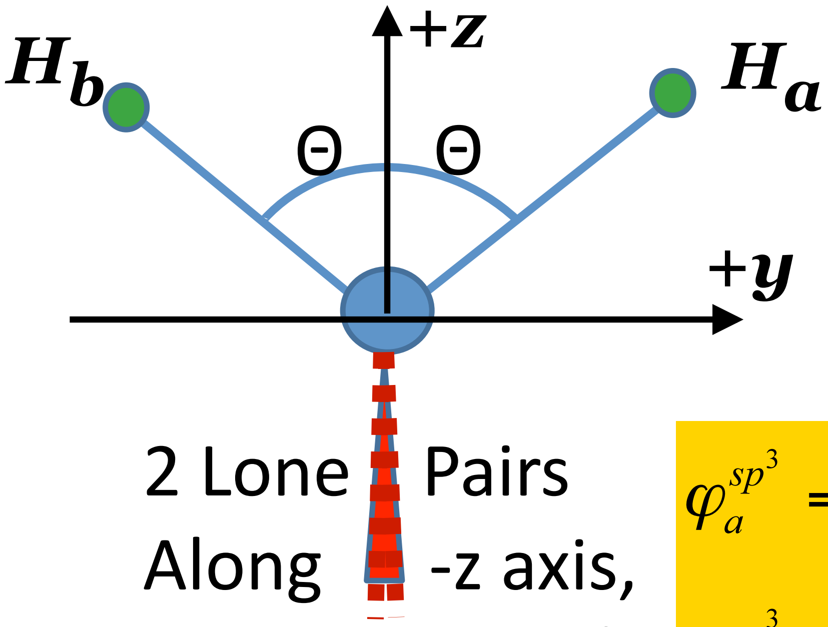
$$\overrightarrow{\varphi_{h3}} \equiv -\frac{1}{\sqrt{6}}\psi_{p_x} + \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

$$\overrightarrow{\varphi_{h2}}.\overrightarrow{\varphi_{h3}} = \left(+\sqrt{\frac{2}{3}}\right)\left(-\frac{1}{\sqrt{6}}\right) + 0.\left(+\frac{1}{\sqrt{2}}\right) + \left(-\frac{1}{2\sqrt{3}}\right)\left(-\frac{1}{2\sqrt{3}}\right) = -\sqrt{\frac{2}{18}} + \frac{1}{12} = -\frac{1}{4}$$

$$\left.\begin{array}{l} |\varphi_{h2}| = \left(\sqrt{\frac{2}{3} + 0 + \frac{1}{12}}\right) = \sqrt{\frac{9}{12}} = \sqrt{\frac{3}{4}} \\ |\varphi_{h3}| = \left(\sqrt{\frac{1}{6} + \frac{1}{2} + \frac{1}{12}}\right) = \sqrt{\frac{9}{12}} = \sqrt{\frac{3}{4}} \end{array}\right\} \rightarrow \boxed{|\varphi_{h2}||\varphi_{h3}| = \frac{3}{4}}$$

$$\cos\theta = \frac{\overrightarrow{\varphi_{h2}}.\overrightarrow{\varphi_{h3}}}{|\varphi_{h2}||\varphi_{h3}|} = -\frac{1}{4} \times \frac{4}{3} = -\frac{1}{3} \quad \rightarrow \quad \theta = 109.5^\circ$$

Non-equivalent Hybrid Orbitals: H_2O



H—O—H angle (2Θ = 104.5)

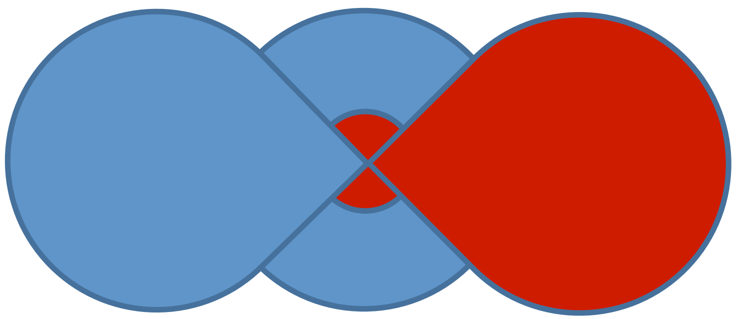
2 H atoms along +z, in yz plane

2 Lone pair of electrons in xz plane (-z)

$$\varphi_a^{sp^3} = N\left[\boxed{\cos\theta}.\psi_{2p_z} + \boxed{\sin\theta}.\psi_{2p_y} - \boxed{\alpha}.\psi_{2s}\right]$$

$$\varphi_b^{sp^3} = N\left[\boxed{\cos\theta}.\psi_{2p_z} - \boxed{\sin\theta}.\psi_{2p_y} - \boxed{\alpha}.\psi_{2s}\right]$$

Why take a negative sign of coefficient for 2s?



Will end up with a "–" sign on each hybrid orbital; which have to form MO with 1s of H (with + sign)

Coefficients of 2 Hybrid Orbitals involved in bonding with H(1s)

$$Hybrid\ orbitals\ are\ Orthogonal:\ 0 = \int \varphi_a^{sp^3} . \varphi_b^{sp^3} d\tau = \left\langle \varphi_a^{sp^3} \middle| \varphi_b^{sp^3} \right\rangle$$

$$= N^2 \left\langle \left[\cos\theta.\psi_{2p_z} + \sin\theta.\psi_{2p_y} - \boxed{\alpha}.\psi_{2s} \right] \middle| \left[\cos\theta.\psi_{2p_z} - \sin\theta.\psi_{2p_y} - \boxed{\alpha}.\psi_{2s} \right] \right\rangle$$

$$0 = N^2 \left[\cos^2\theta \left\langle \psi_{2p_z} \middle| \psi_{2p_z} \right\rangle - \sin^2\theta \left\langle \psi_{2p_y} \middle| \psi_{2p_y} \right\rangle + \alpha^2 \left\langle \psi_{2s} \middle| \psi_{2s} \right\rangle \right]$$

$$N^2 \left[\cos^2\theta - \sin^2\theta + \alpha^2 \right] = N^2 \left[\cos 2\theta + \alpha^2 \right] = 0$$

$$\rightarrow \boxed{\cos 2\theta = -\alpha^2 \rightarrow 180^\circ \geq 2\theta \geq 90^\circ}\ (Consistent!)$$

$$In\ H_2O,\ \ H-O-H\ angle: 2\theta = 104.5^\circ \rightarrow \theta = 52.25^\circ$$

$$\varphi_a^{sp^3} = N\left[\boxed{0.61}.\psi_{2p_z} + \boxed{0.79}.\psi_{2p_y} - \boxed{0.50}.\psi_{2s} \right]$$

$$\varphi_b^{sp^3} = N\left[\boxed{0.61}.\psi_{2p_z} - \boxed{0.79}.\psi_{2p_y} - \boxed{0.50}.\psi_{2s} \right]$$

Normalize each bonding-hybrids to obtain correct coefficients

$$Normalize \rightarrow 1 = \int \varphi_a^{sp^3} . \varphi_a^{sp^3} d\tau = \left\langle \varphi_a^{sp^3} \middle| \varphi_a^{sp^3} \right\rangle$$

$$1 = N^2 \left[(0.61)^2 \left\langle \psi_{2p_z} \middle| \psi_{2p_z} \right\rangle + (0.79)^2 \left\langle \psi_{2p_y} \middle| \psi_{2p_y} \right\rangle + (0.50)^2 \left\langle \psi_{2s} \middle| \psi_{2s} \right\rangle \right]$$

$$N^2 = 1 \Big/ \left[(0.61)^2 + (0.79)^2 + (0.50)^2 \right] \quad \rightarrow \quad N = 0.89$$

$$\varphi_a^{sp^3} = 0.55\psi_{2p_z} + 0.71\psi_{2p_y} - 0.45\psi_{2s}$$

$$\varphi_b^{sp^3} = 0.55\psi_{2p_z} - 0.71\psi_{2p_y} - 0.45\psi_{2s}$$

% P character: $(0.55)^2+(0.71)^2=0.80$ (80%)

% S character = $(-0.45)^2 = 0.2$ (20%)

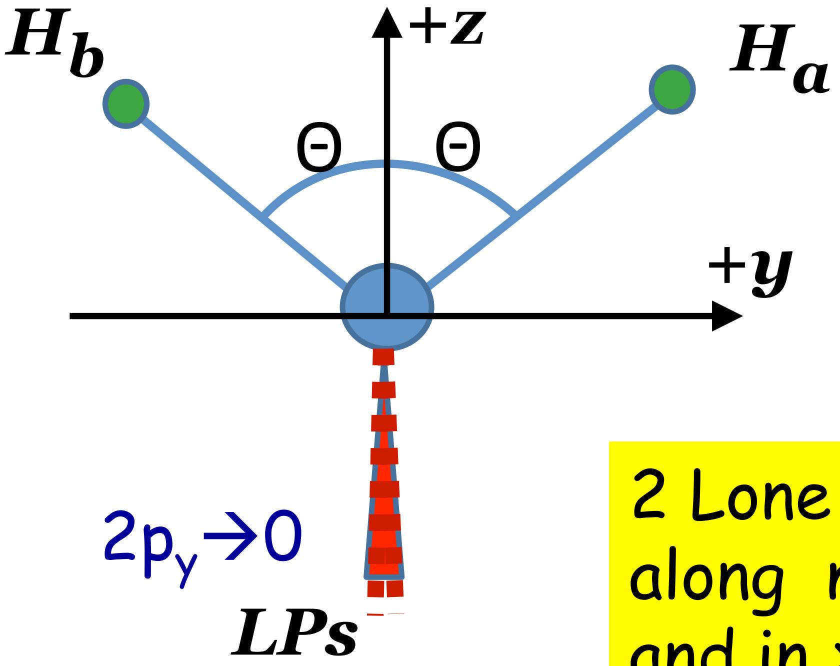
➔ **more like SP4 , rather than SP3**

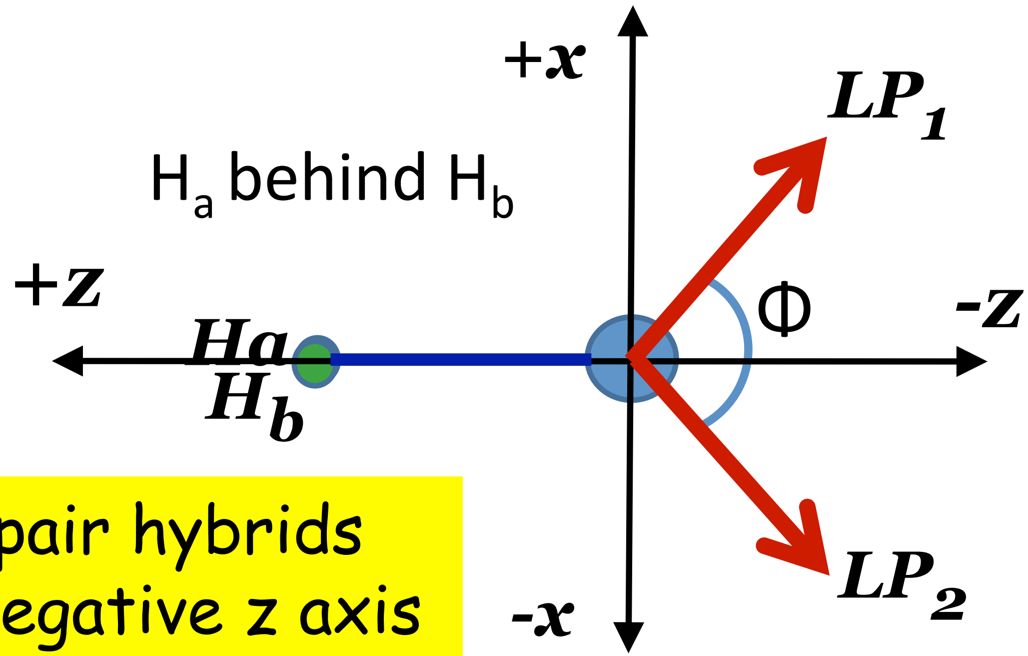
What happens to the lone pairs of electrons?

Lone-pair hybrid orbitals will have different coefficients!

$$\varphi_{lp1}^{sp^3} = d_1.\psi_{2p_z} + d_2.\psi_{2p_y} + d_3.\psi_{2s} + d_4.\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_5.\psi_{2p_z} + d_6.\psi_{2p_y} + d_7.\psi_{2s} + d_8.\psi_{2p_x}$$





2 Lone pair hybrids along negative z axis and in xz plane - No contribution from p_y

Lone-pair hybrid orbitals will have different coefficients!

$$\varphi_{lp1}^{sp^3} = d_1 \psi_{2p_z} + d_2 \psi_{2p_y} + d_3 \psi_{2s} + d_4 \psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_5 \psi_{2p_z} + d_6 \psi_{2p_y} + d_7 \psi_{2s} + d_8 \psi_{2p_x}$$

Because lone-pairs are directed along x-z plane: d2=d6=0

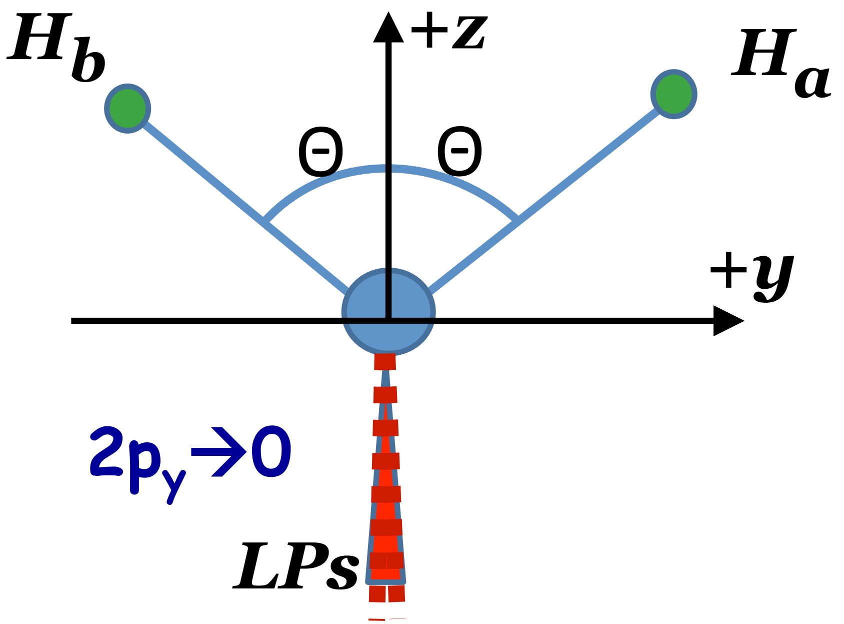
$$\varphi_{lp1}^{sp^3} = d_1 \psi_{2p_z} + 0\psi_{2p_y} + d_3 \psi_{2s} + d_4 \psi_{2p_x}$$

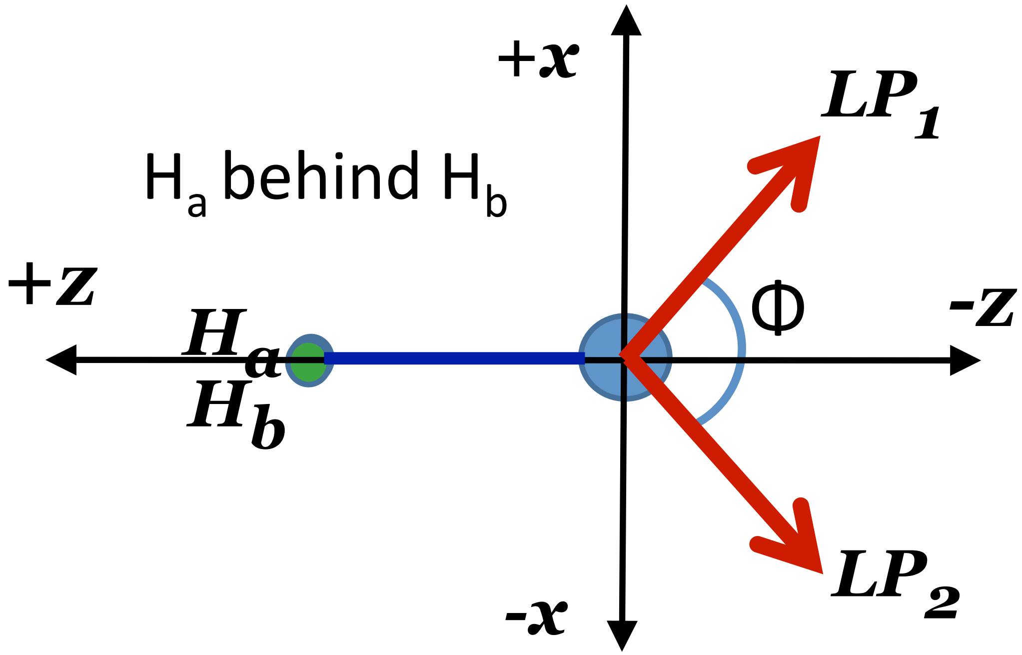
$$\varphi_{lp2}^{sp^3} = d_5 \psi_{2p_z} + 0\psi_{2p_y} + d_7 \psi_{2s} + d_8 \psi_{2p_x}$$

Other's contributions (using symmetry)

S : Same for both LP hybrid orbitals: d3 = d7
$2p_Z$:Same for both LP hybrids: d5 = d1
2px: Same magnitude, opposite in sign: d8 = -d4

Use symmetry to equate coefficients





$2p_z \rightarrow d5 = d1$ $\quad$ $S \rightarrow d3 = d7$ $\quad$ $2p_x \rightarrow d8 = -d4$

$$\varphi_{lp1}^{sp^3} = d_1\psi_{2p_z} + 0\psi_{2p_y} + d_3\psi_{2s} + d_4\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_1\psi_{2p_z} + 0\psi_{2p_y} + d_3\psi_{2s} - d_4\psi_{2p_x}$$

Total contributions of s, p_x, p_y, p_z is unity considering all four hybrids

For 2 lone-pair hybrid orbitals:

$$\varphi_{lp1}^{sp^3} = d_1\psi_{2p_z} + 0\psi_{2p_y} + d_3\psi_{2s} + d_4\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_1\psi_{2p_z} + 0\psi_{2p_y} + d_3\psi_{2s} - d_4\psi_{2p_x}$$

For bonded hybrid orbitals:

$$\varphi_{a}^{sp^3} = 0.55\psi_{2p_z} + 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

$$\varphi_{b}^{sp^3} = 0.55\psi_{2p_z} - 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

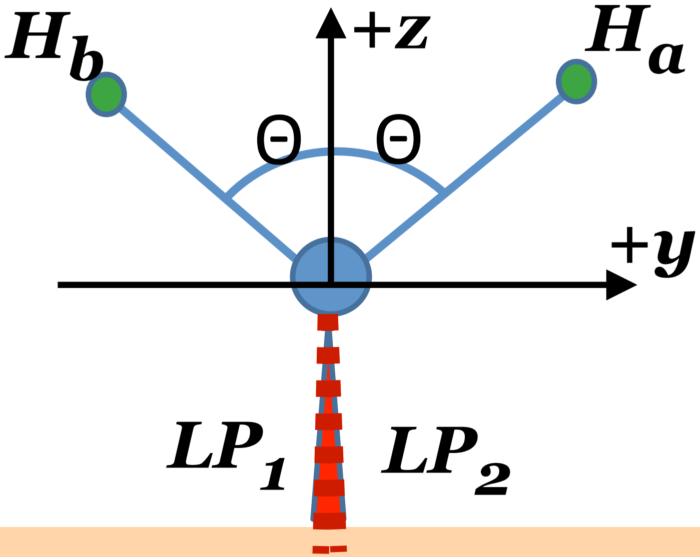
For $2p_z$ $\quad d_1^2 + d_1^2 + (0.55)^2 + (0.55)^2 = 1 \rightarrow d_1 = \pm 0.45$

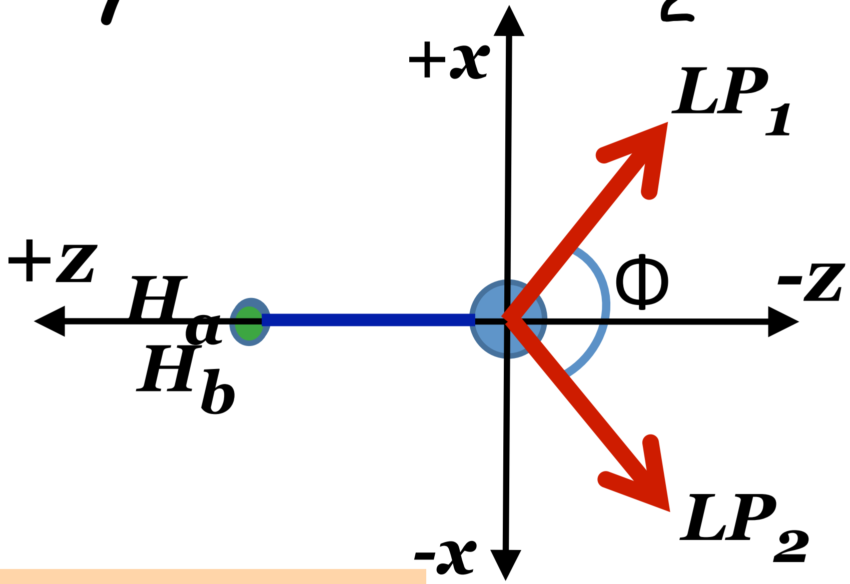
For $2p_y$ $\quad (0)^2 + (0)^2 + (0.71)^2 + (0.71)^2 = 1$ *(done before)*

For 2s $\quad d_3^2 + d_3^2 + (0.45)^2 + (0.45)^2 = 1 \rightarrow d_3 = \pm 0.55$

For $2p_x$ $\quad d_4^2 + d_4^2 + (0)^2 + (0)^2 = 1 \rightarrow d_4 = \pm 0.71$

Different s-/p- character for the two classes of hybrids in H_2O





$$\varphi_{lp1}^{sp^3} = -0.45\psi_{2p_z} - 0.55\psi_{2s} + 0.71\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = -0.45\psi_{2p_z} - 0.55\psi_{2s} - 0.71\psi_{2p_x}$$

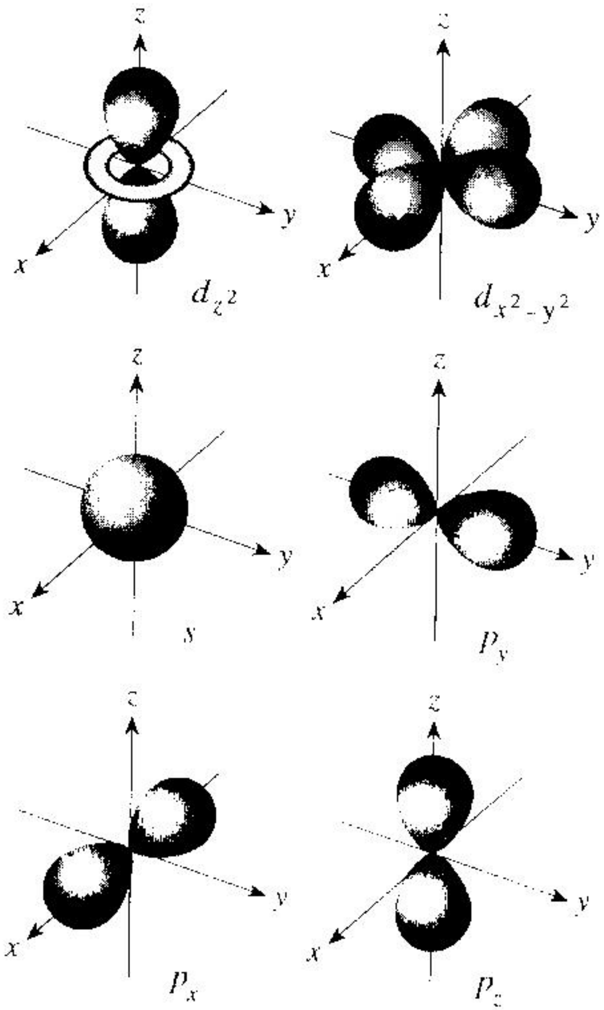
S ➔ $(0.55)^2$ → 30%
P ➔ 100-30 → 70%

$$\varphi_{a}^{sp^3} = 0.55\psi_{2p_z} + 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

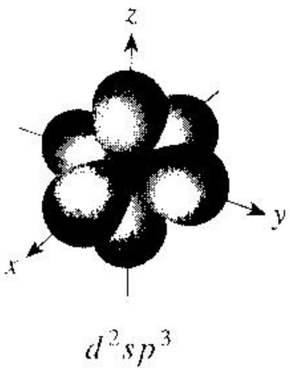
$$\varphi_{b}^{sp^3} = 0.55\psi_{2p_z} - 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

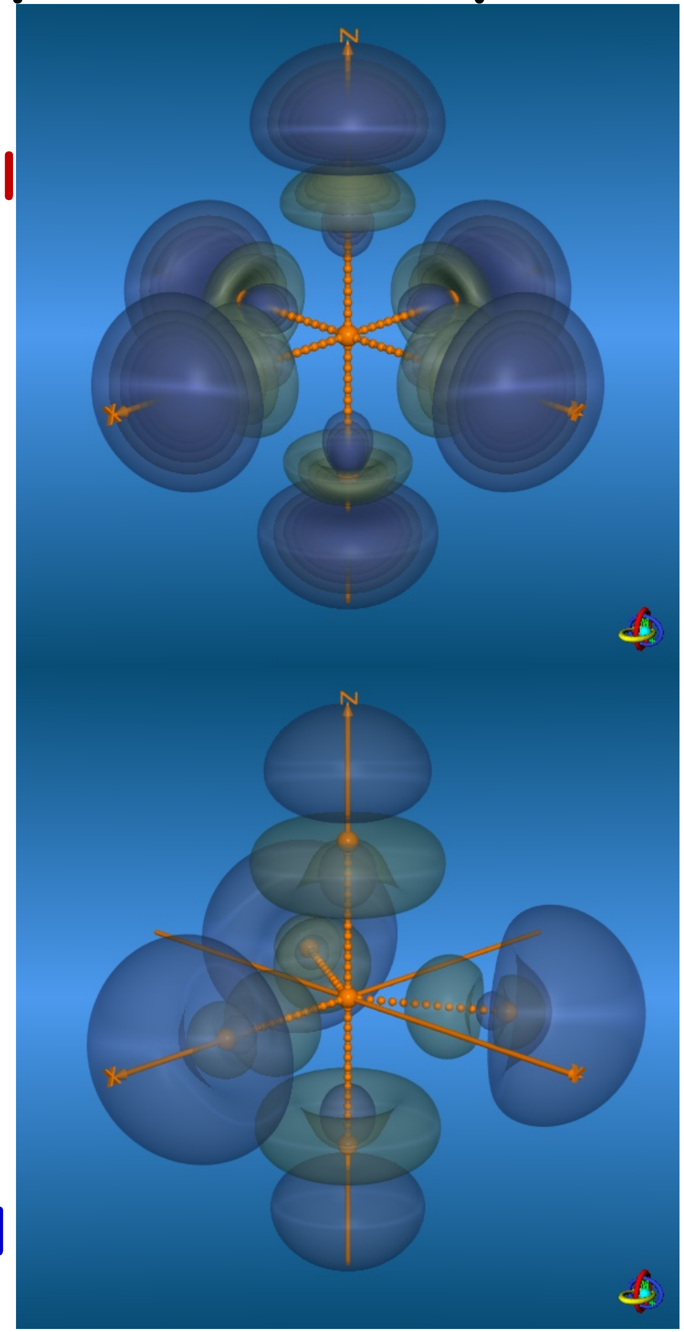
S ➔ 20%
P ➔ 80%

Hybridization of s,p,d: sp^3d^2 and sp^3d



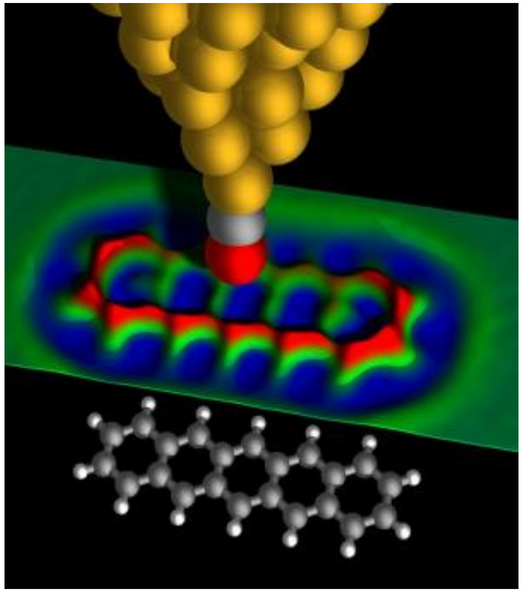
Sp^3d^2: octahedral

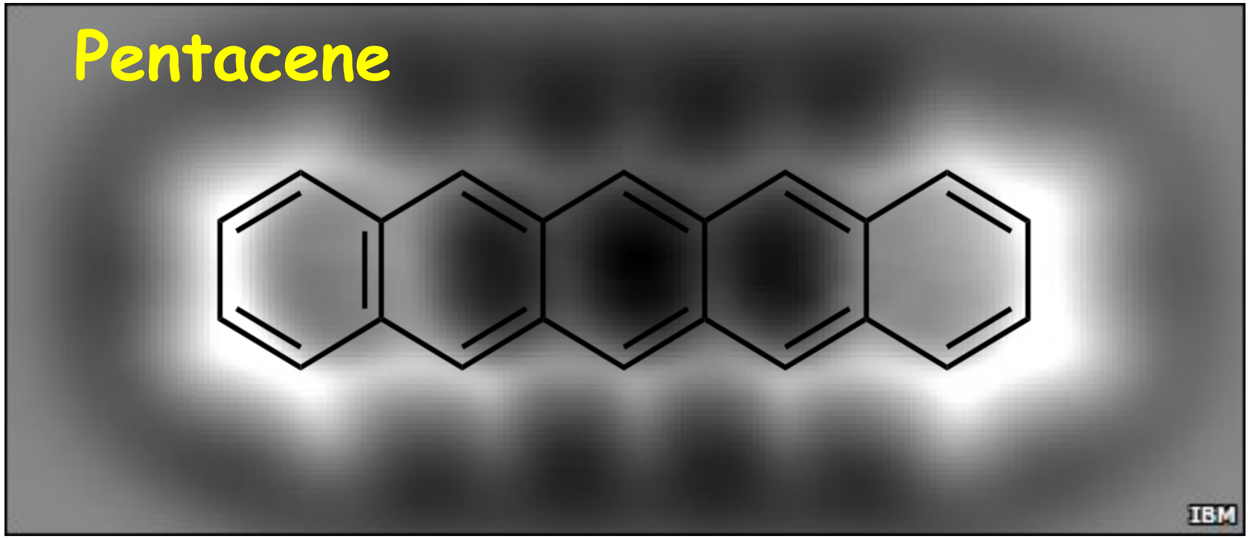


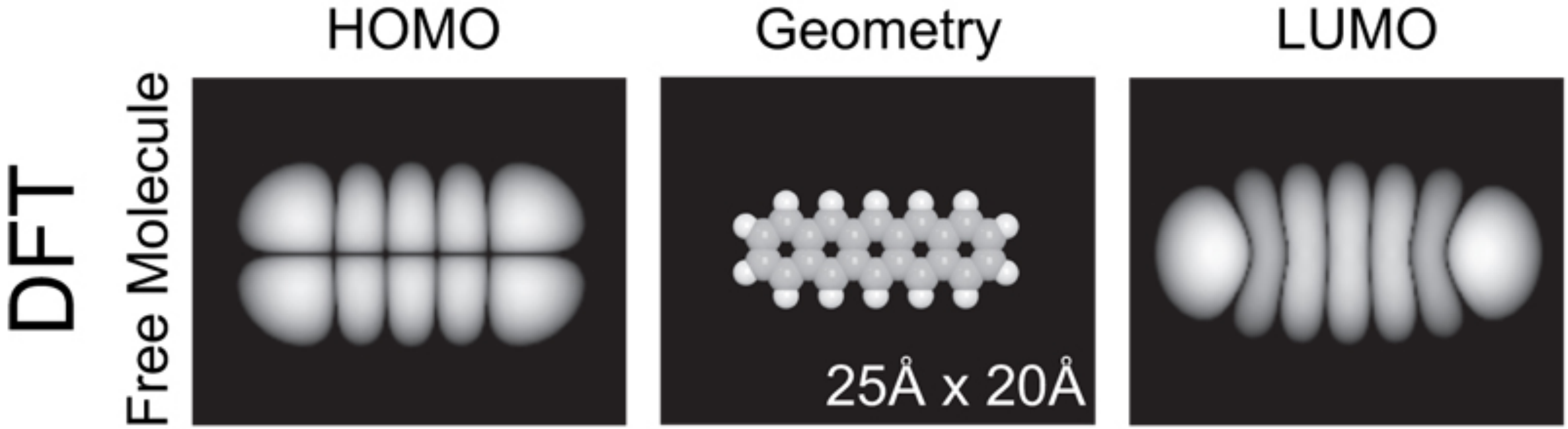


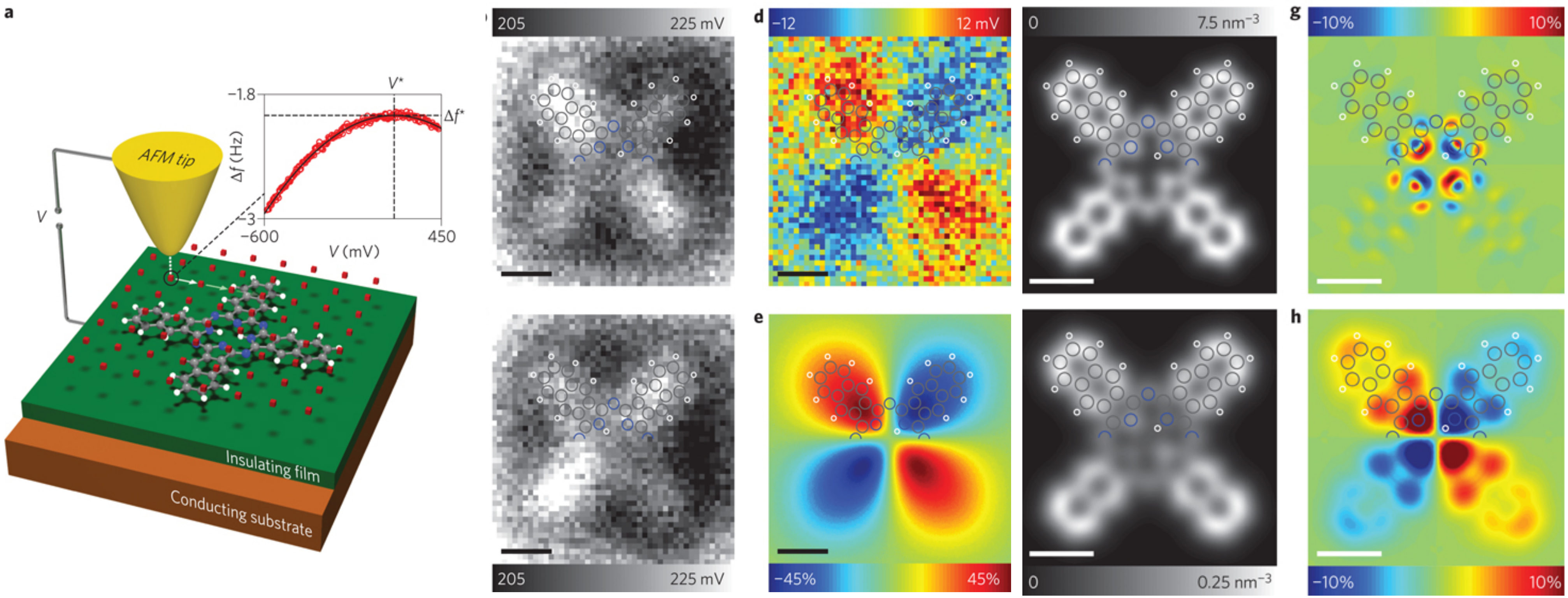
Similarly, sp^3d → trigonal bipyramidal

Experimental mapping of electron density (or MO) for individual molecules









Collaboration of engineers and scientists has led to such fantastic discoveries

C_{60}: Fullerene