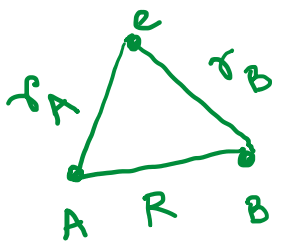
Simplest possible molecule ⇝ H_2^+ (Hydrogen molecule ion)



Two nuclei are kept fixed

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}$$

- $\hat{H}$ ↓ Hamiltonian operator
- ① ↳ K.E. of electron
- $\frac{e^2}{4\pi\varepsilon_0 r_A} + \frac{e^2}{4\pi\varepsilon_0 r_B}$ ↳ e^--nuclei attraction.
- $\frac{e^2}{4\pi\varepsilon_0 R}$ ← nucleus-nucleus repulsion

Difficult to solve exactly? ⇝ Can be solved exactly in elliptical co-ordinate system

We will rather do variational calculation in a.u

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

Trial wavefⁿ (in general) $\Phi = c_A \psi_{1s_A} + c_B \psi_{1s_B}$ ⇝ LCAO (linear combination of atomic orbitals)

close to nucleus A ⇝ like a H-atom ⇝ $\psi_{1s_A} = \frac{1}{\sqrt{\pi}} e^{-r_A}$

" " B ⇝ " " ⇝ $\psi_{1s_B} = \frac{1}{\sqrt{\pi}} e^{-r_B}$

} Atomic Orbitals (real fⁿs)

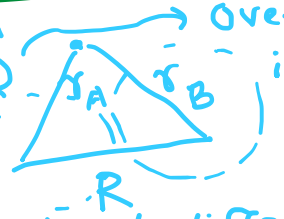
$$\mathcal{E} = \frac{\int d\tau \, \Phi^* \hat{H} \Phi}{\int d\tau \, \Phi^* \Phi} \rightsquigarrow = \frac{\int d\tau \, (c_A \psi_{1s_A} + c_B \psi_{1s_B}) \hat{H} (c_A \psi_{1s_A} + c_B \psi_{1s_B})}{\int d\tau \, (c_A \psi_{1s_A} + c_B \psi_{1s_B})(c_A \psi_{1s_A} + c_B \psi_{1s_B})}$$

$$= \frac{c_A^2 \int d\tau \, \psi_{1s_A} \hat{H} \psi_{1s_A} + c_B^2 \int d\tau \, \psi_{1s_B} \hat{H} \psi_{1s_B} + c_A c_B \int d\tau \, \psi_{1s_A} \hat{H} \psi_{1s_B} + c_B c_A \int d\tau \, \psi_{1s_B} \hat{H} \psi_{1s_A}}{c_A^2 \int \psi_{1s_A} \psi_{1s_A} d\tau + c_B^2 \int d\tau \, \psi_{1s_B} \psi_{1s_B} + 2 c_A c_B \int \psi_{1s_A} \psi_{1s_B} d\tau}$$

H_{AA} H_{BB} H_{AB} H_{BA}

$\int \psi_{1s_A} \psi_{1s_A} d\tau \to 1$ $\int d\tau \, \psi_{1s_B} \psi_{1s_B} \to 1$

$\int \psi_{1s_A} \psi_{1s_B} d\tau \neq 0$ — overlap integral



wavefⁿs corresponding to different nuclei

$$\varepsilon = \frac{c_A^2 H_{AA} + c_B^2 H_{BB} + c_A c_B H_{AB} + c_B c_A H_{BA}}{c_A^2 + c_B^2 + 2 c_A c_B S} \geq E_0$$

$$H_{AB} = \int d\tau \, \psi_{1s_A} \hat{H} \psi_{1s_B}$$

$\hat{H} \rightarrow$ Hermitian

$$H_{BA} = \int d\tau \, \psi_{1s_B} \hat{H} \psi_{1s_A} \rightarrow H_{AB} = H_{BA}$$

$\int d\tau \, \psi_A^* \hat{H} \psi_B = \left(\int d\tau \, \psi_B^* \hat{H} \psi_A \right)^*$

When ψ_A, ψ_B are real

$\int d\tau \, \psi_A H \psi_B = \int d\tau \, \psi_B H \psi_A$

$$\varepsilon (c_A^2 + c_B^2 + 2 c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB}$$

↓ Differentiating with respect to c_A

$$\frac{\partial \varepsilon}{\partial c_A} (c_A^2 + c_B^2 + 2 c_A c_B S) + \varepsilon (2 c_A + 2 c_B S) = 2 c_A H_{AA} + 2 c_B H_{AB}$$

$\frac{\partial \varepsilon}{\partial c_A} = 0$; $\frac{\partial \varepsilon}{\partial c_B} = 0$

↓

$$\varepsilon (c_A + c_B S) = c_A H_{AA} + c_B H_{AB}$$

$$\Rightarrow c_A (H_{AA} - \varepsilon) + c_B (H_{AB} - \varepsilon S) = 0 \quad \cdots (1)$$

$$\varepsilon(c_A^2 + c_B^2 + 2c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B H_{AB}$$

$$\frac{\partial \varepsilon}{\partial c_B}(c_A^2 + c_B^2 + 2c_A c_B S) + \varepsilon(2c_B + 2c_A S) = 2c_B H_{BB} + 2c_A H_{AB}$$

$$\Rightarrow \quad \varepsilon(c_B + c_A S) = c_B H_{BB} + c_A H_{AB}$$

$$c_A(H_{AA} - \varepsilon) + c_B(H_{AB} - \varepsilon S) = 0 \quad \cdots (1)$$

eqn

$$\Rightarrow \quad c_A(H_{AB} - \varepsilon S) + c_B(H_{BB} - \varepsilon) = 0 \quad \cdots (2)$$

$$\begin{bmatrix} H_{AA} - \varepsilon & H_{AB} - \varepsilon S \\ H_{AB} - \varepsilon S & H_{BB} - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

$\underline{\underline{A}}\,\underline{C} = \underline{0}$ ← (null matrix)

$\underline{\underline{A}}^{-1}\underline{\underline{A}}\,\underline{C} = \underline{0} \Rightarrow \underline{C} = \underline{0}$

$\underline{\underline{A}}^{-1}\underline{\underline{A}}$ = $\underline{\underline{I}}$ (Unity Matrix)

$c_A = 0, c_B = 0$ (wavefn will vanish)

$|A| = 0$ ← A^{-1} does not exist

$$\begin{vmatrix} H_{AA}-\varepsilon & H_{AB}-\varepsilon S \\ H_{AB}-\varepsilon S & H_{BB}-\varepsilon \end{vmatrix} = 0$$

$|A| = 0$ → Determinant

$$H_{AA} = \int d\tau \psi_{1s_A} \hat{H} \psi_{1s_A} \quad ; \quad H_{BB} = \int d\tau \psi_{1s_B} \hat{H} \psi_{1s_B}$$

Expectation values of $\hat{H}$

$$(H_{AA}-\varepsilon)^2 - (H_{AB}-\varepsilon S)^2 = 0$$

$H_{AA} = H_{BB}$ (Homonuclear diatomic)

$$\Rightarrow (H_{AA}-\varepsilon) = (H_{AB}-\varepsilon S)$$

$$(H_{AA}-\varepsilon) = -(H_{AB}-\varepsilon S)$$

$$\varepsilon = \frac{H_{AA}-H_{AB}}{1-S}$$

$$\varepsilon = \frac{H_{AA}+H_{AB}}{1+S}$$

this is lower in energy!! H_{AB} is negative (can be shown)

Calculate C_A, C_B

$C_A = C_B$

$C_A = -C_B$

Full Hamiltonian for H_2^+ (a.u)

$M \sim 1837\, m$

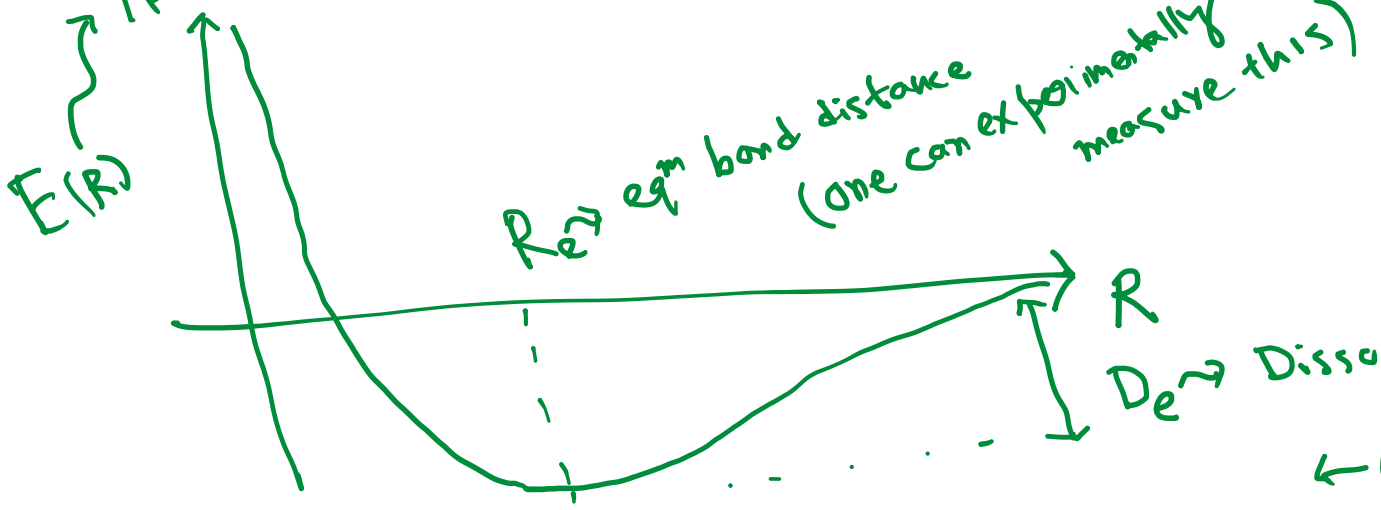
$$\hat{H} = -\frac{1}{2\times 1837}\nabla_A^2 - \frac{1}{2\times 1837}\nabla_B^2 - \frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

$$\simeq -\frac{\nabla^2}{2} - \frac{1}{r_A} + \frac{1}{R} - \frac{1}{r_B}$$

Small and can be ignored

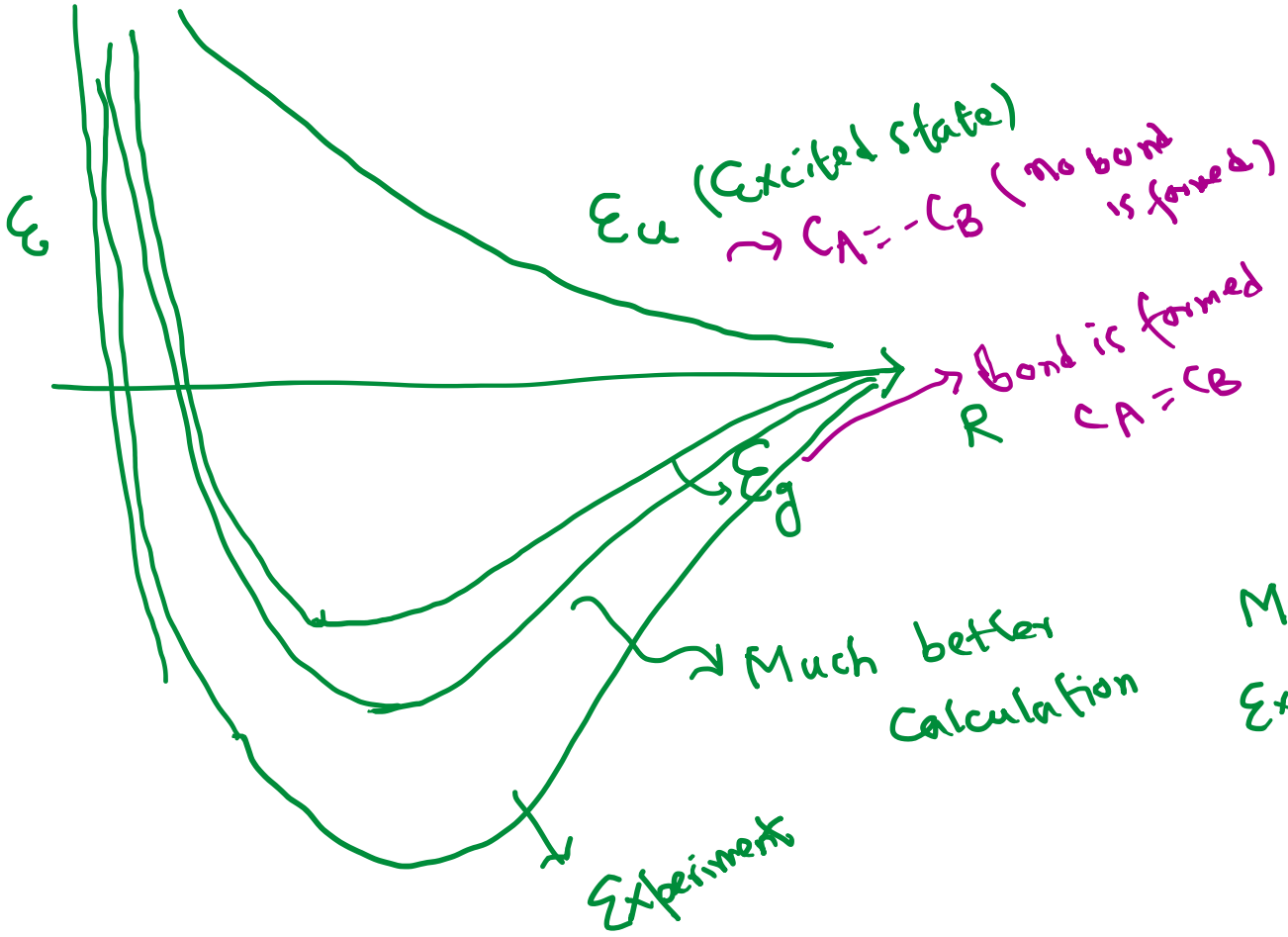
→ nuclei are sluggish (kept fixed)

⇝ Born-Oppenheimer approximation



$E(R)$ ↓ internuclear distance

← Chemical bond → $\bar{e}$ being shared by two nuclei



$$E_g = \frac{H_{AA} + H_{AB}}{1+S}$$

$$E_u = \frac{H_{AA} - H_{AB}}{1-S}$$

H_2^+	Re	De
MO	1.32 Å	1.77 eV
Expt	1.06 Å	2.77 eV

H_{AA}, H_{AB} & S $\rightsquigarrow$ can be calculated analytically (elliptical co-ordinates)

$$H_{AA} = -\frac{1}{2} + e^{-2R}(1+R) \qquad H_{AB} = \left(-\tfrac{1}{2} + \tfrac{1}{R}\right)S + \delta$$

$$\delta = e^{-R}(1+R)$$

$$S = e^{-R}(1+R)$$

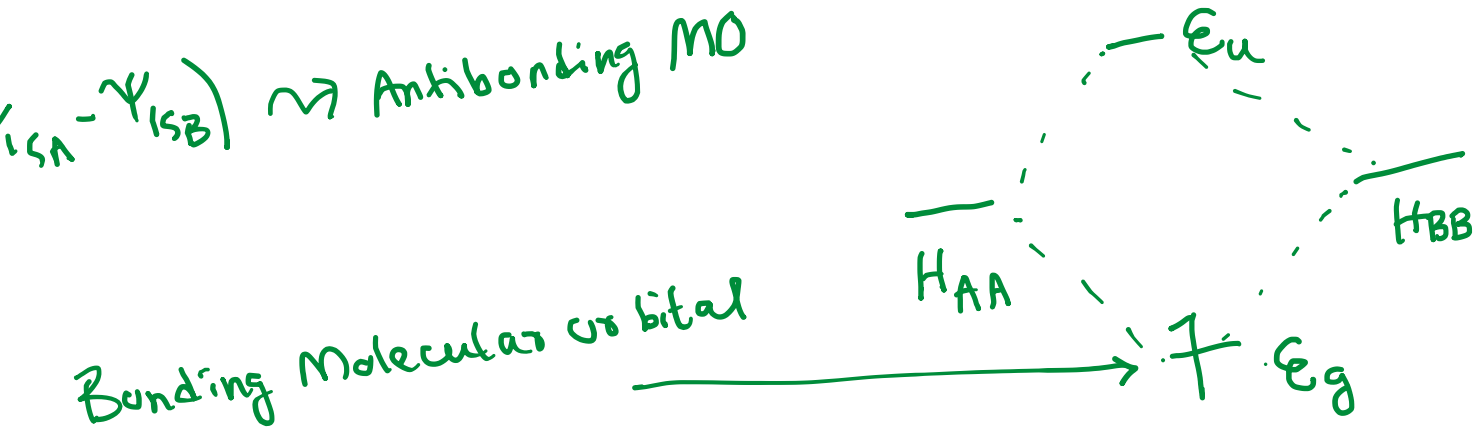
C_A & C_B? $\int (C_A\psi_{1sA} + C_A\psi_{1sB})^2 d\tau = 1 \rightsquigarrow C_A^2 \underbrace{\int \psi_{1sA}\psi_{1sA} d\tau}_{1} + C_A^2 \underbrace{\int \psi_{1sB}\psi_{1sB} d\tau}_{1} + 2C_A^2 S = 1$

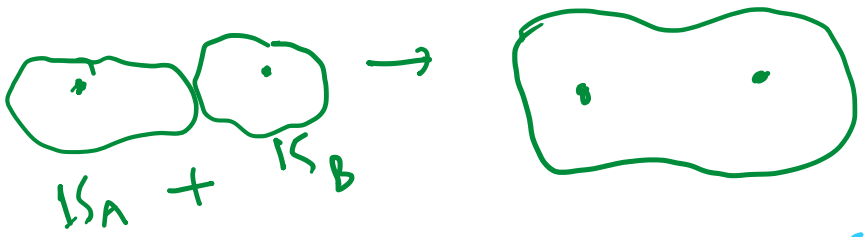
$2C_A^2(1+S) = 1 \Rightarrow$

$$C_A = \frac{1}{\sqrt{2(1+S)}}$$

$$\phi_g = \frac{1}{\sqrt{2(1+S)}}(\psi_{1sA} + \psi_{1sB}) \rightsquigarrow \text{Bonding MO}$$

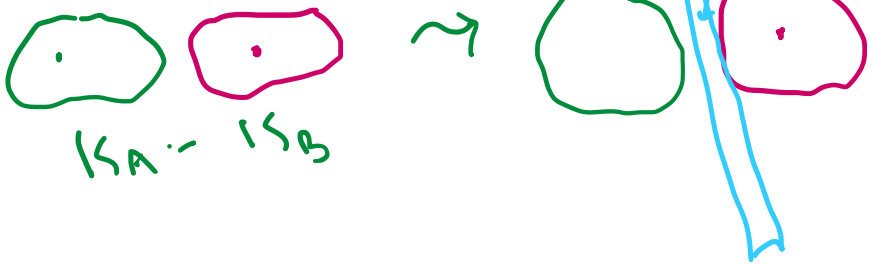
$$\phi_u = \frac{1}{\sqrt{2(1-S)}}(\psi_{1sA} - \psi_{1sB}) \rightsquigarrow \text{Antibonding MO}$$





→ No node(s)

$$\frac{1}{\sqrt{2(1+S)}}(\psi_{1s_A} + \psi_{1s_B})$$



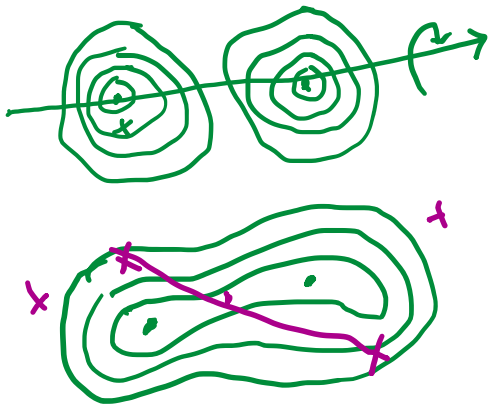
~ Energy is higher

$$\frac{1}{\sqrt{2(1-S)}}(\psi_{1s_A} - \psi_{1s_B})$$

$$S = e^{-R}(1+R)$$

$R \to \infty$ $\quad S = 0$

$R = 0$ $\quad S = 1$



Cylindrical symmetry

σ type orbital

No change in sign ~ "gerade"

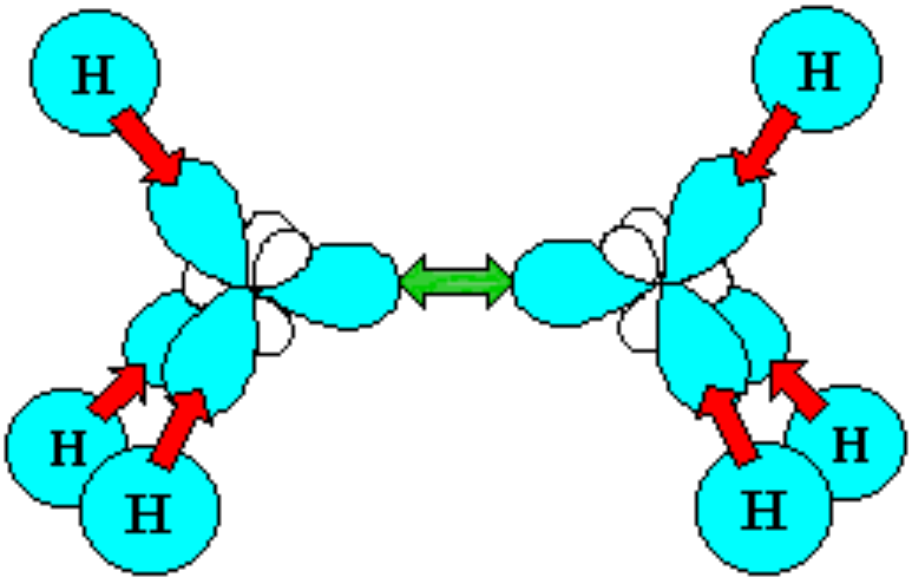
→ Antisymmetric

Sign changes (ungerade)

σ_{g1s} (Bonding)

σ^*_{u1s} ← higher in energy

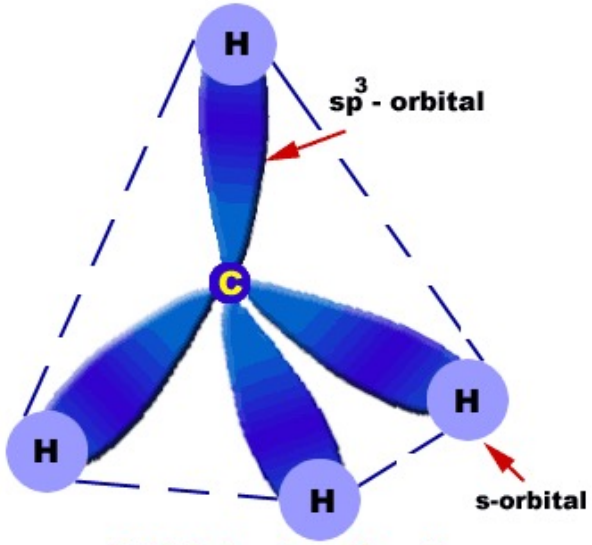
Bonding in Polyatomic molecules



Hybridization !!

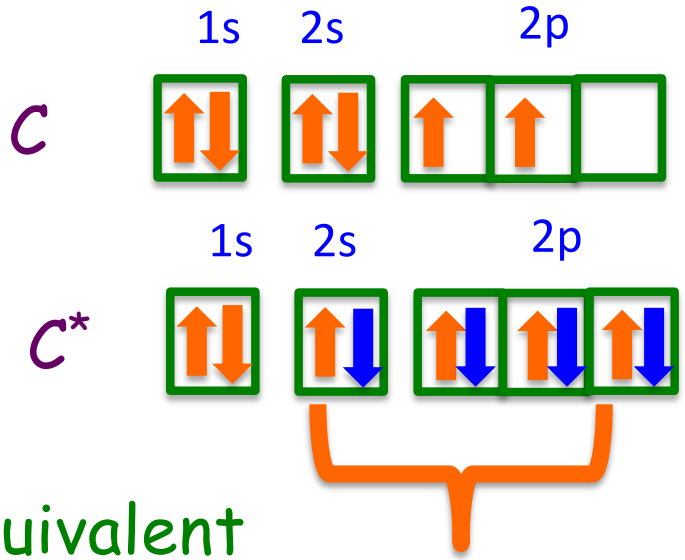
In chemistry, hybridization is the concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties.

What we learnt in +2 or CH 105?



Orbital structure of methane

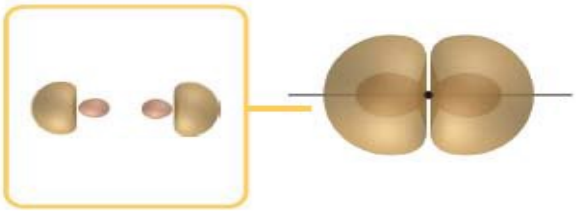
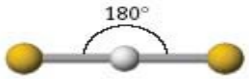
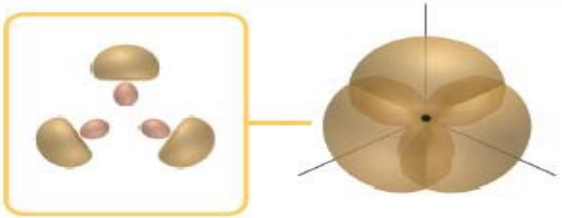
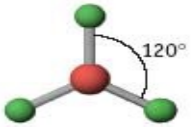
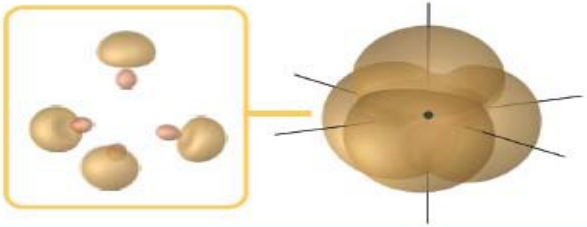
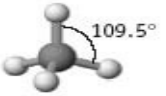
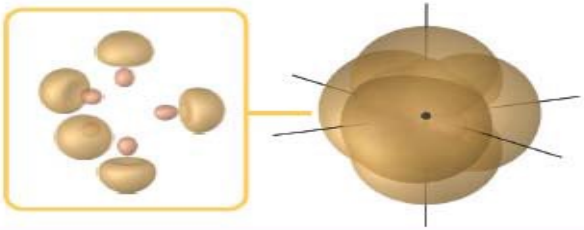
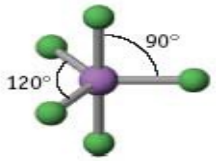
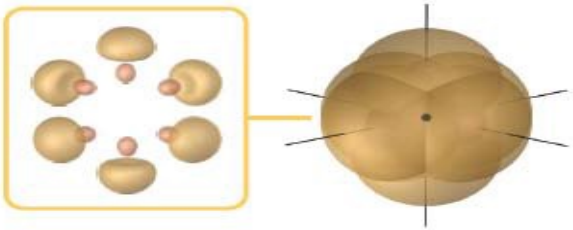
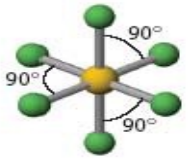
Carbon in ground state



Four equivalent hybrid orbitals

sp^3

Hybridization and Geometry

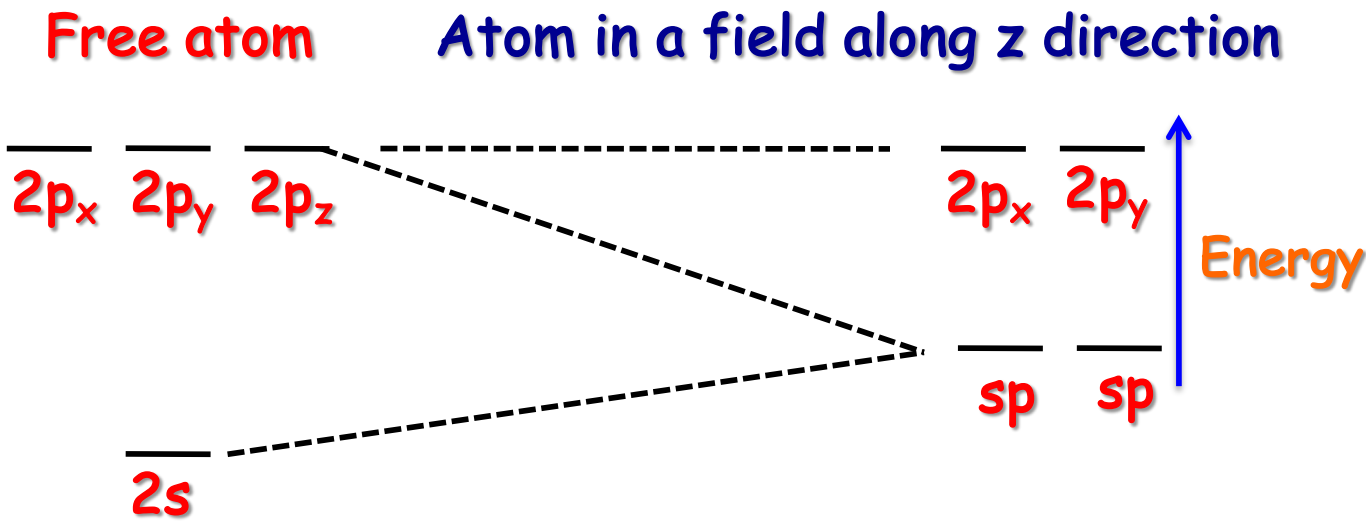
Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs *sp*		Linear	 $BeCl_2$
Three electron pairs sp^2		Trigonal-planar	 BF_3
Four electron pairs sp^3		Tetrahedral	 CH_4
Five electron pairs sp^3d		Trigonal-bipyramidal	 PF_5
Six electron pairs sp^3d^2		Octahedral	 SF_6

Hybrids: Linear Combination of s and p leads to lowering of energy

Linus Pauling, ~1930

Hybrid Orbital's

- Linear combination of atomic orbital's within an atom leading to more effective bonding situation



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

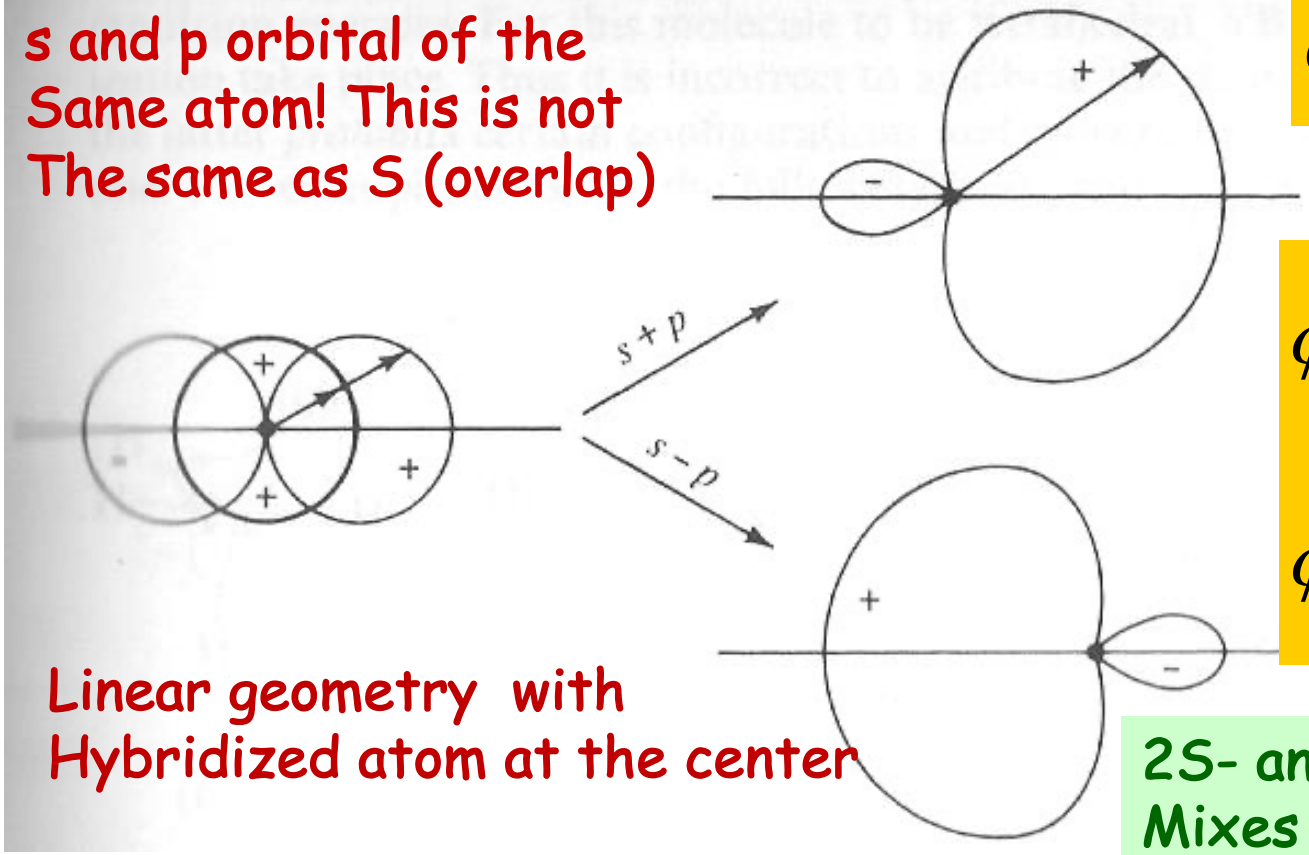
Linear Environment: s & 1-p mix: sp

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)



Linear geometry with Hybridized atom at the center

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

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

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

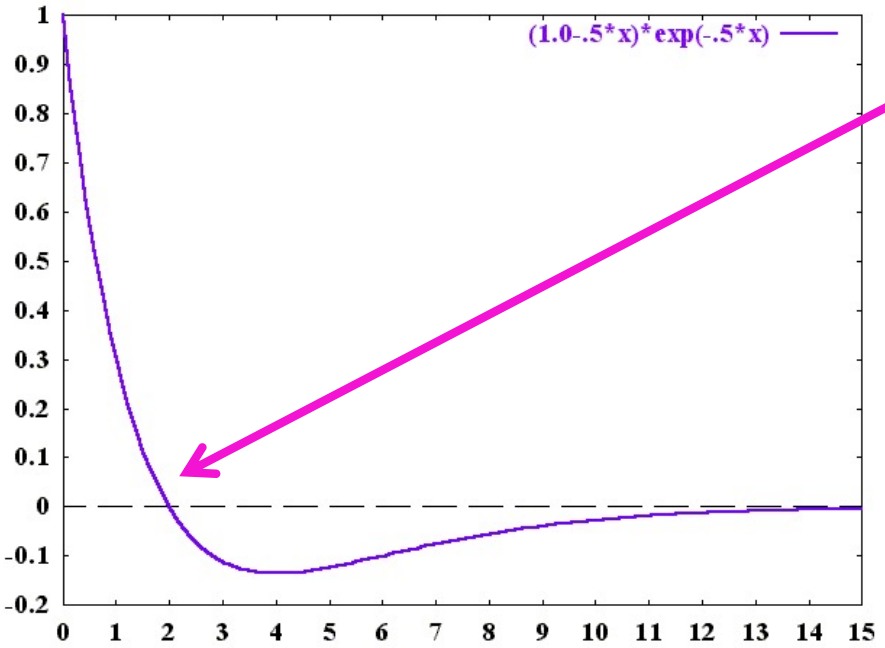
2s orbital

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

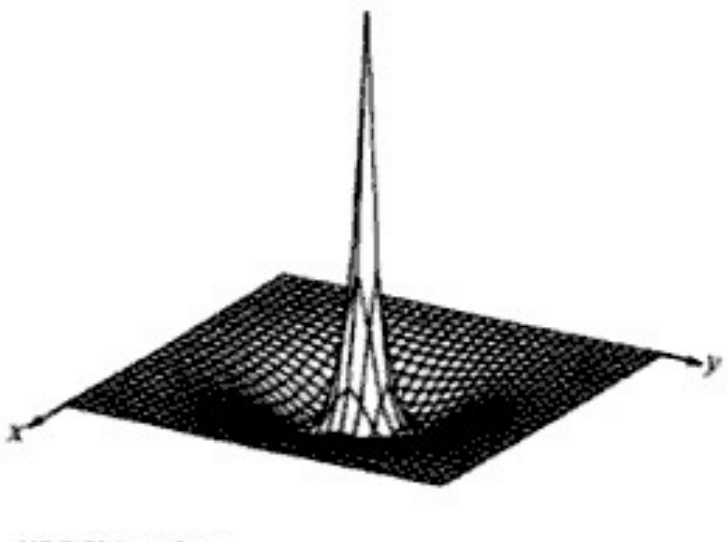
radial node

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

$$\frac{R_{2s}}{(1/\sqrt{2})(Z/a)^{\frac{3}{2}}}$$

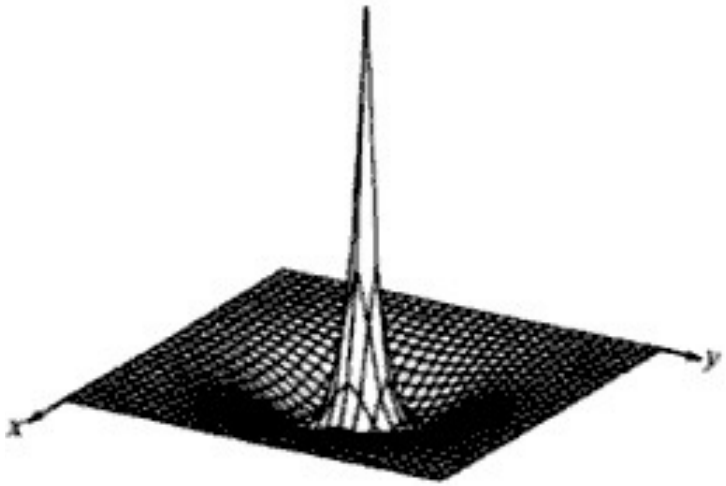


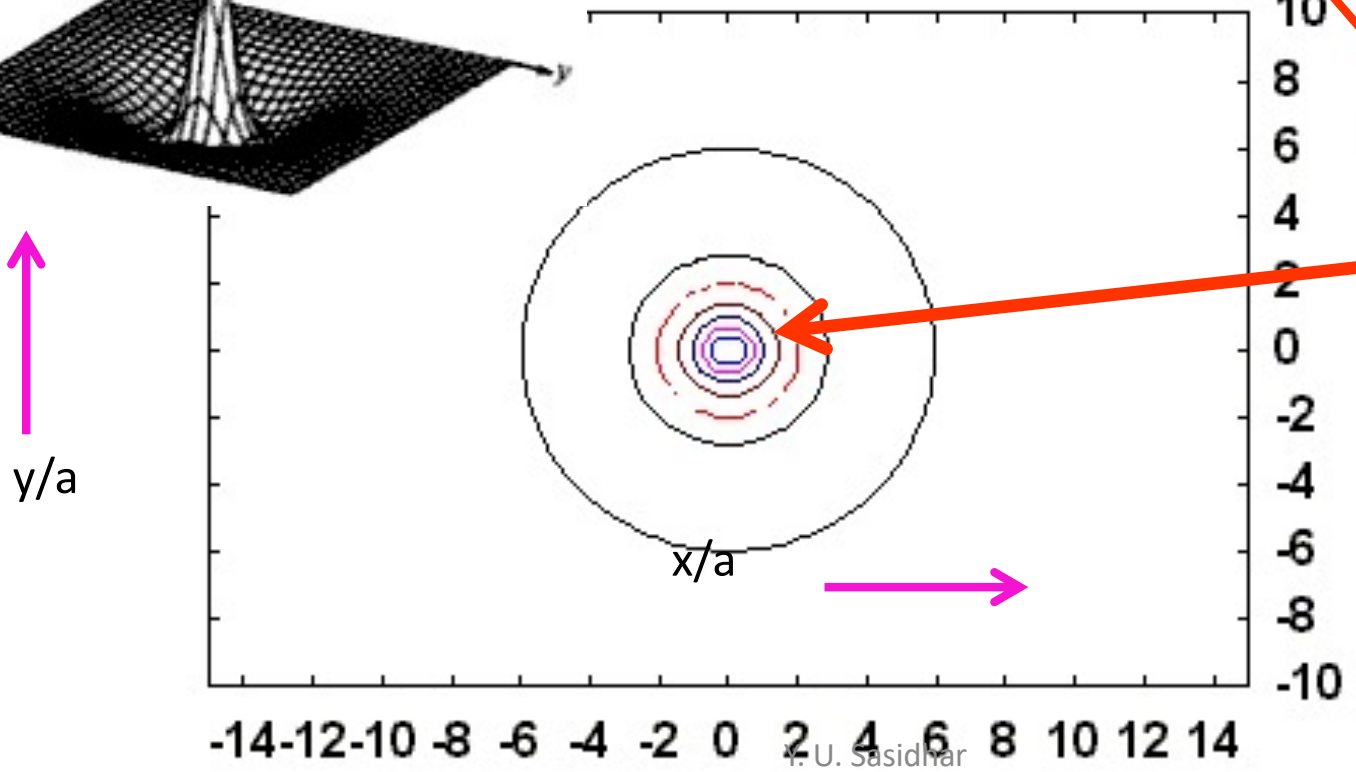
$r / a \longrightarrow$



2s orbital

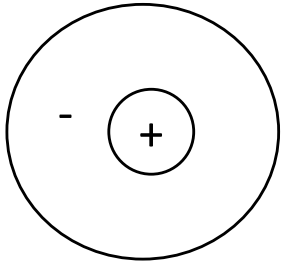
$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^{0}\left(2 - \frac{Zr}{a}\right)\exp(-Zr/2a)$$





$: \frac{2a}{Z}$

radial node



$2p_z$ orbital

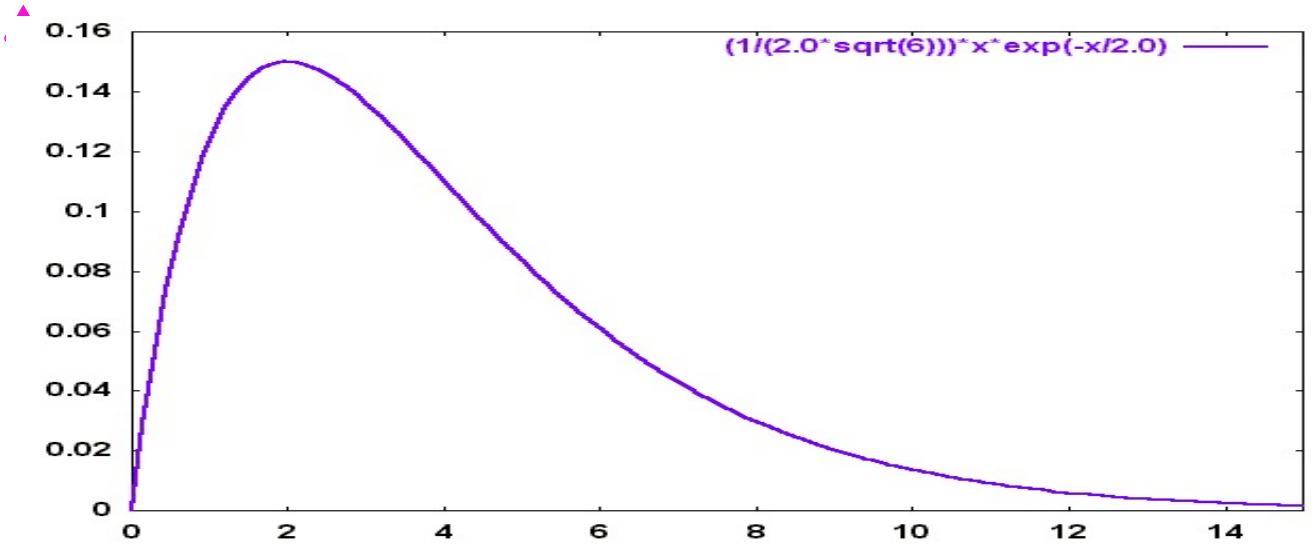
$$\Psi_{\substack{2p_z \\ (2,1,0)}} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r^{1} \exp(-Zr/2a)\cos\theta$$

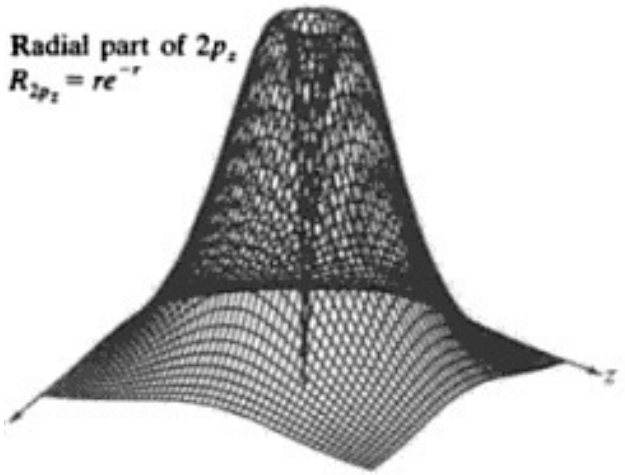
Angular Part

$\cos\theta = z/r$

Radial Part starts with a zero at r=0; so does Ψ

$$R_{2p}a^{3/2} = (1/2\sqrt{6})Z^{5/2}(r/a)\exp(-Zr/2a)$$





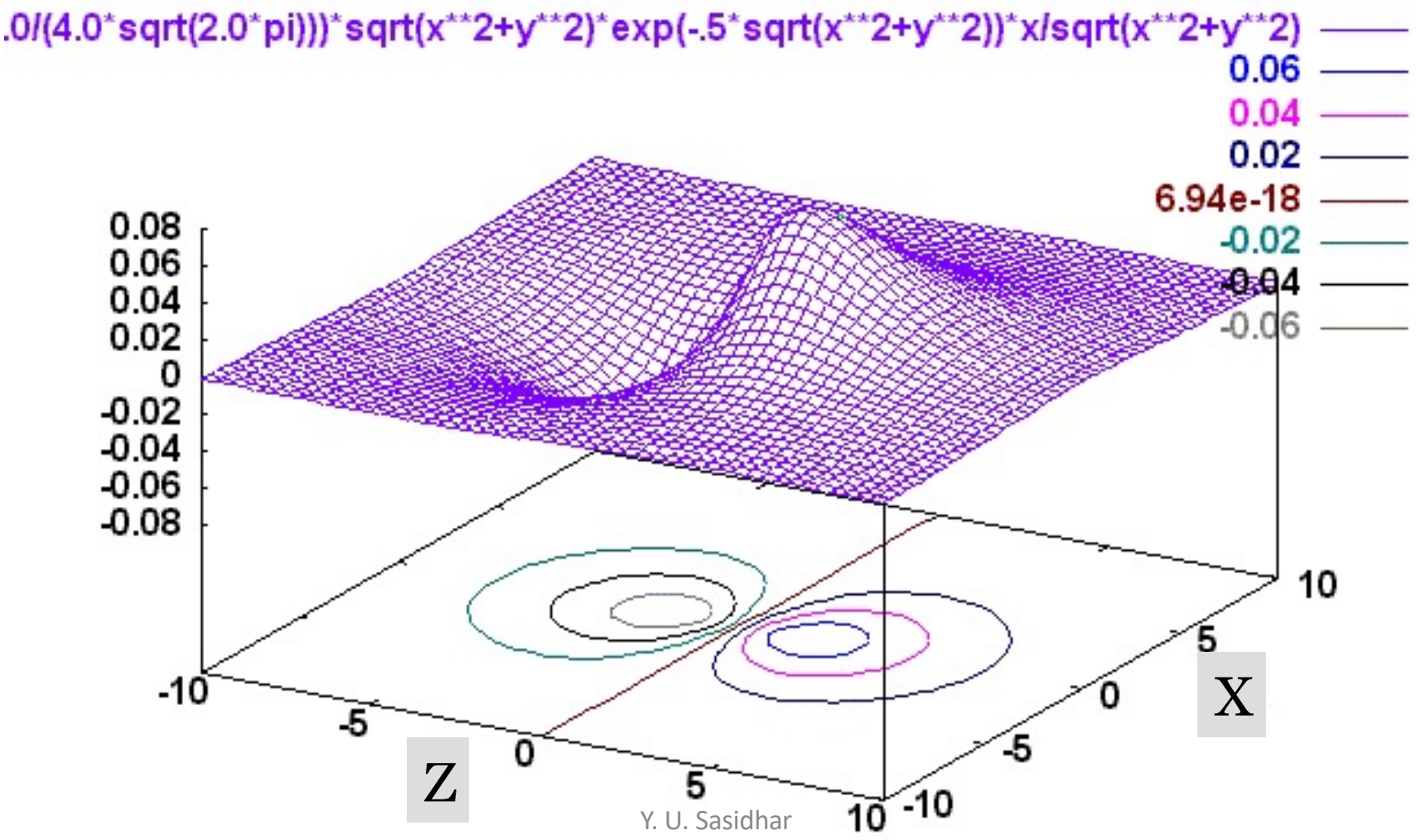
$r/a \rightarrow$

$2p_z$ orbital

$$\Psi_{\substack{2p_z \\ (2,1,0)}} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} \underline{\underline{r^1}} \exp(-Zr/2a)\cos\theta$$

Angular Part

$\cos\theta = z/r$

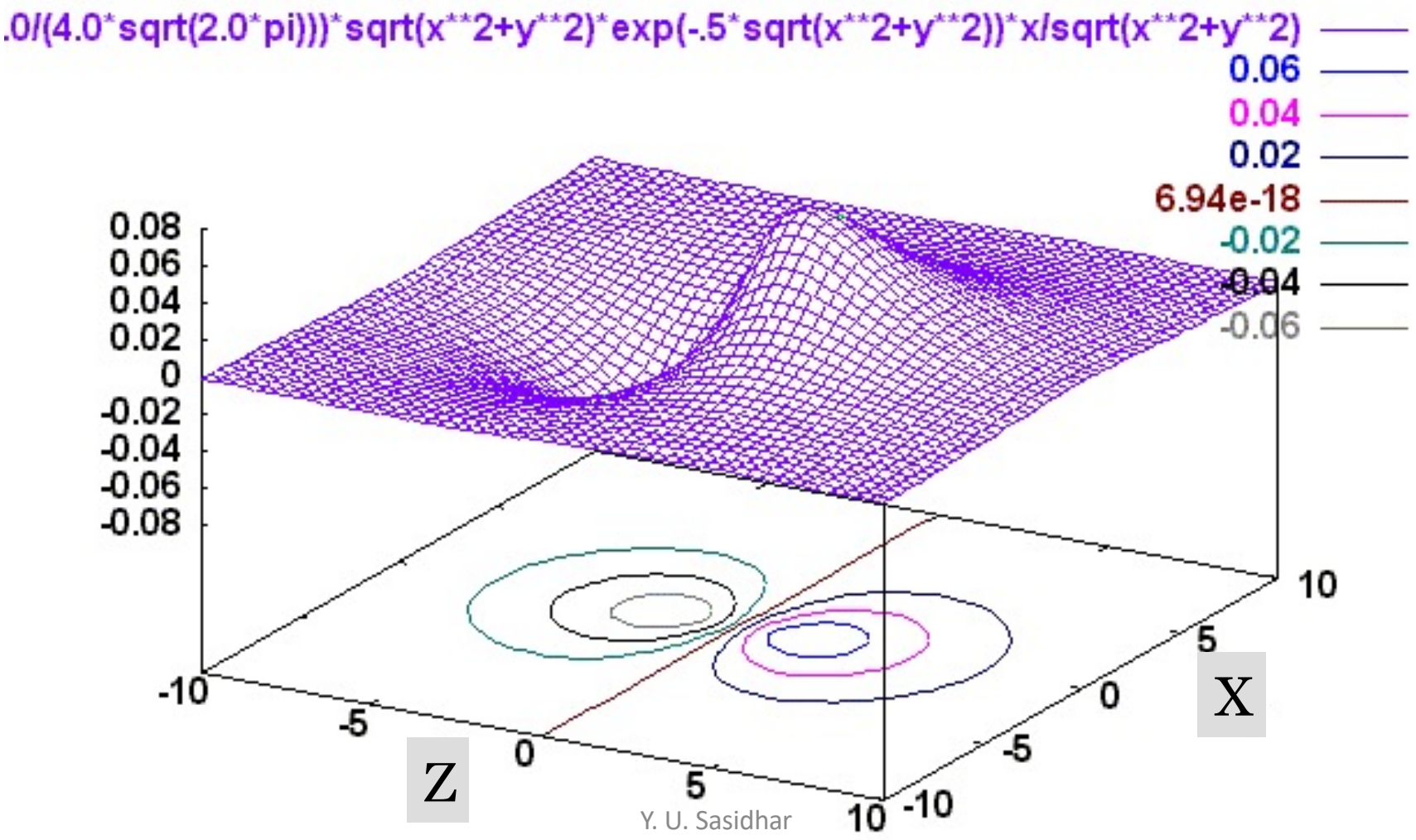


$2p_z$ orbital

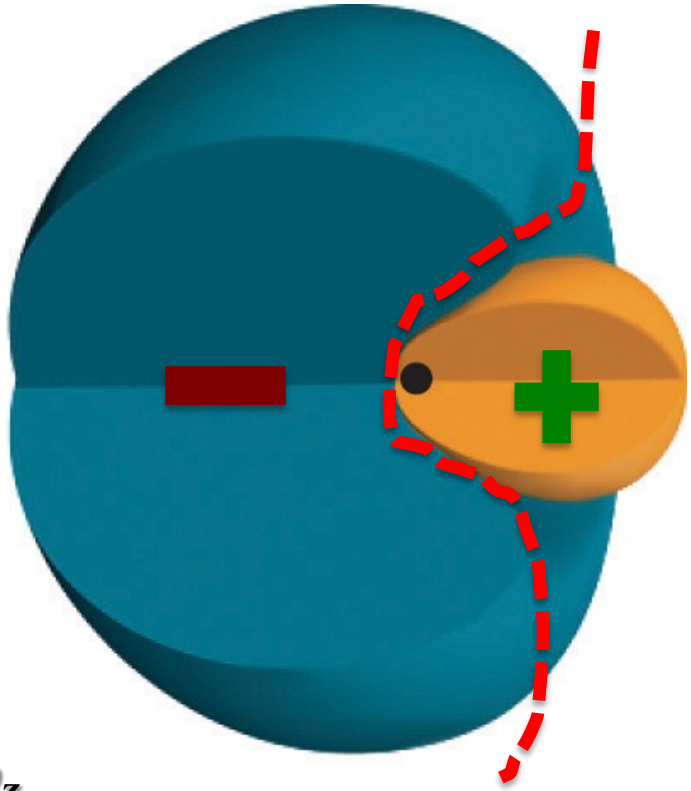
$$\Psi_{\substack{2p_z \\ (2,1,0)}} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} \underline{\underline{r^1}} \exp(-Zr/2a)\cos\theta$$

Angular Part

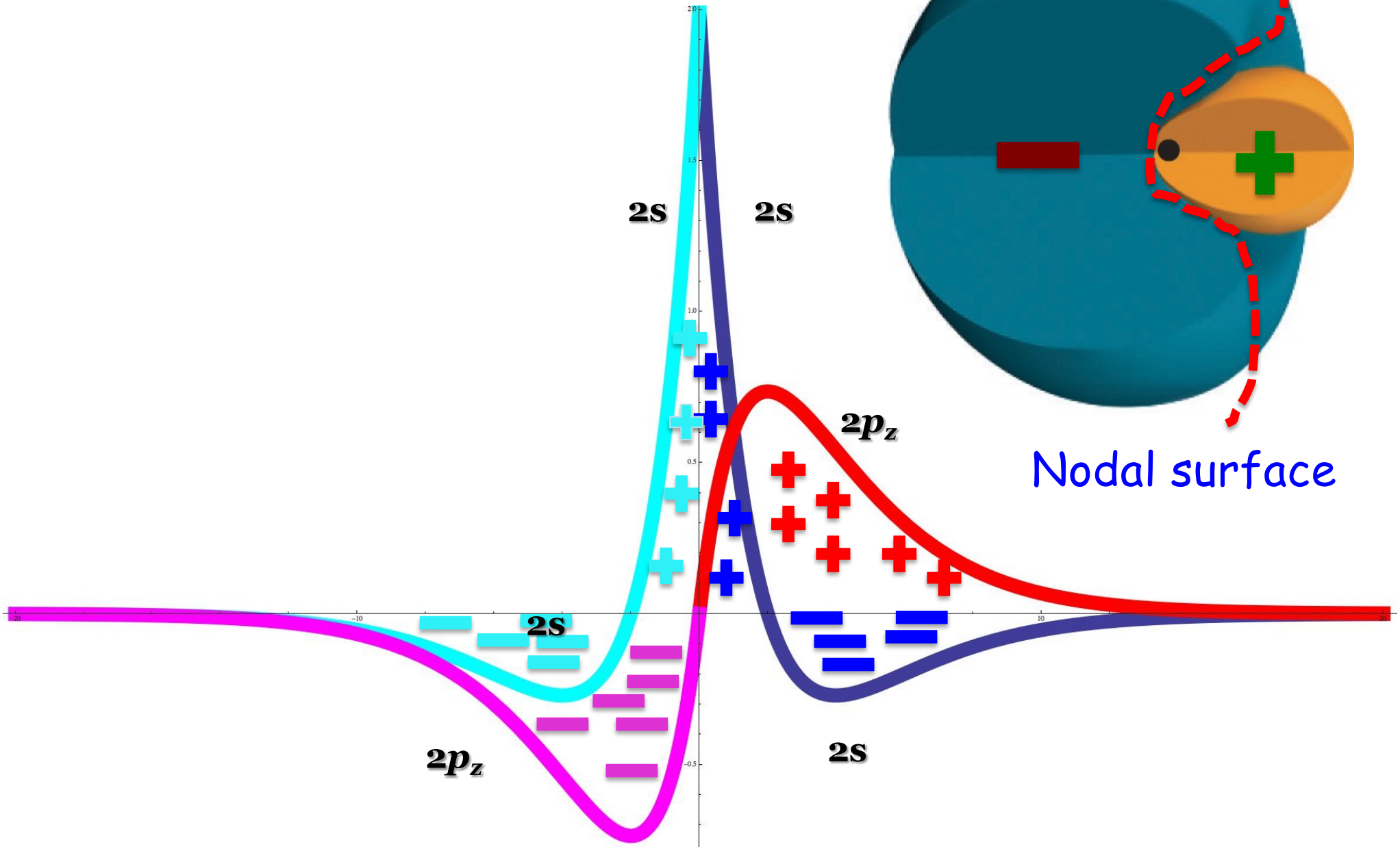
$\cos\theta = z/r$



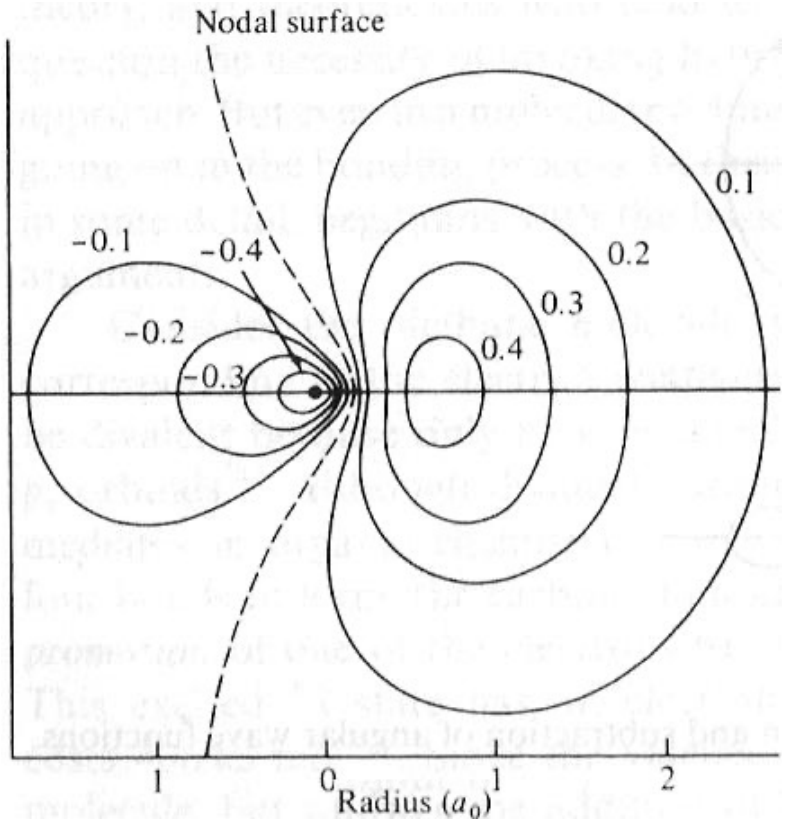
Sections of the orbitals

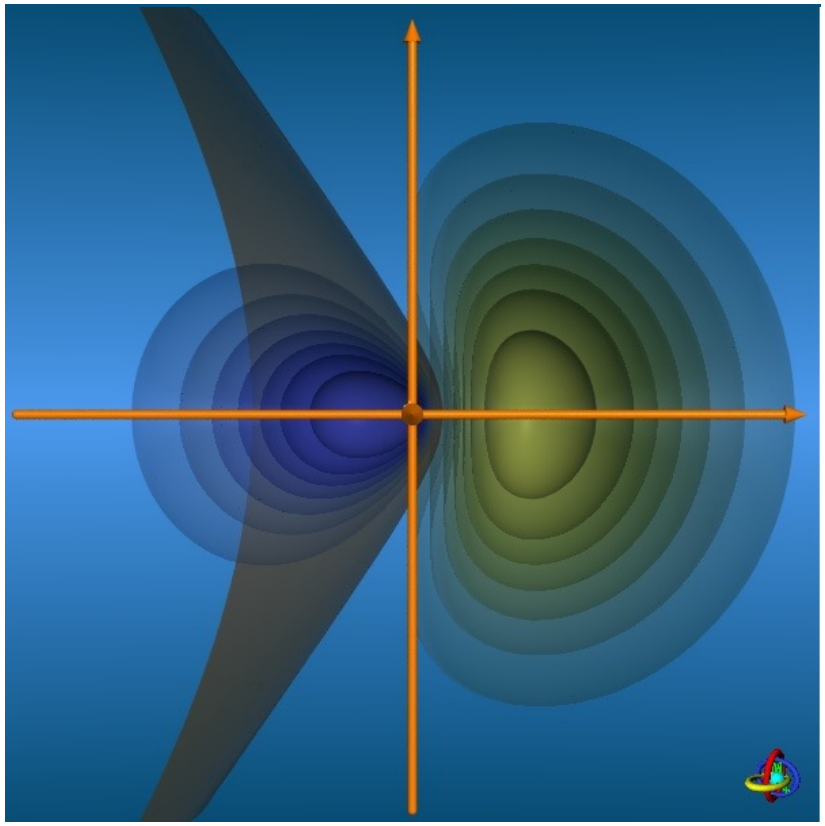


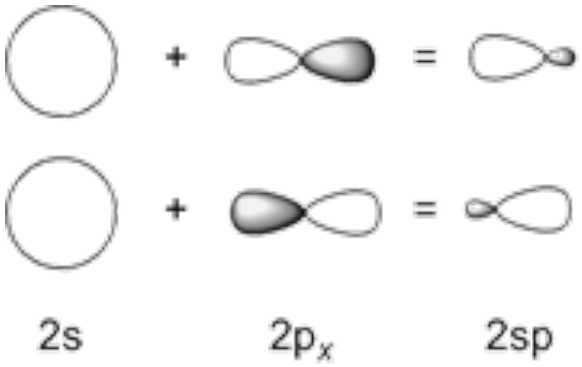
Nodal surface



Contours & bonding of sp-hybridization

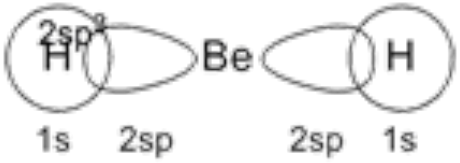




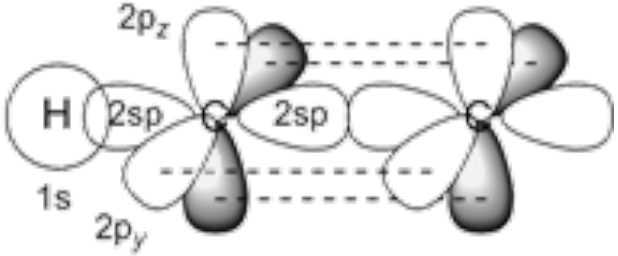


2 more p-orbital available for bonding

Examples:



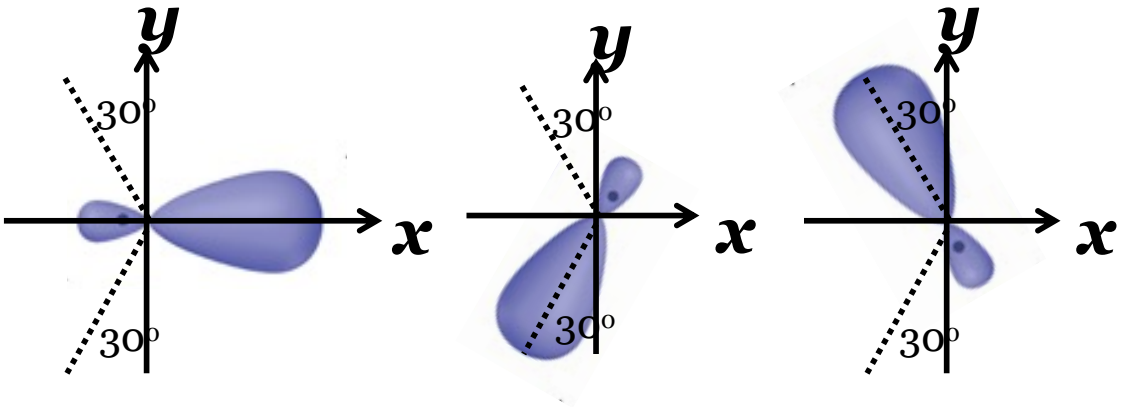
BeH_2 H-Be–H

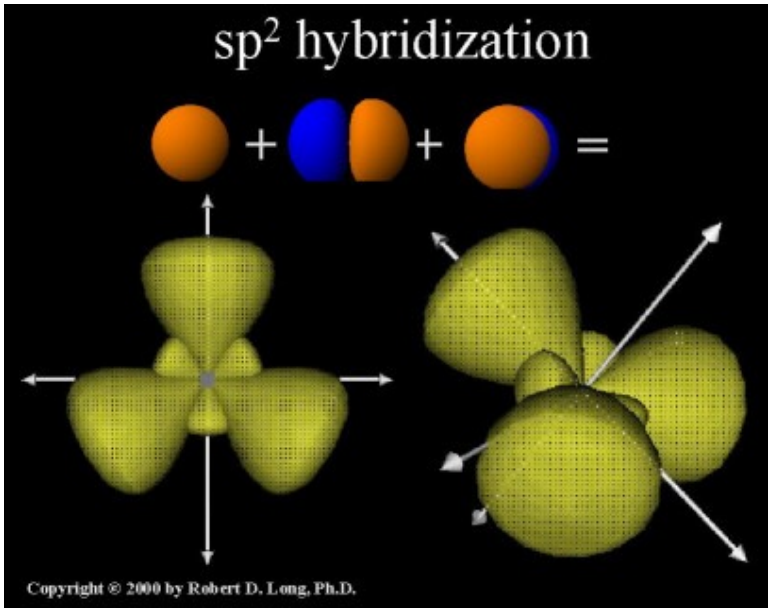


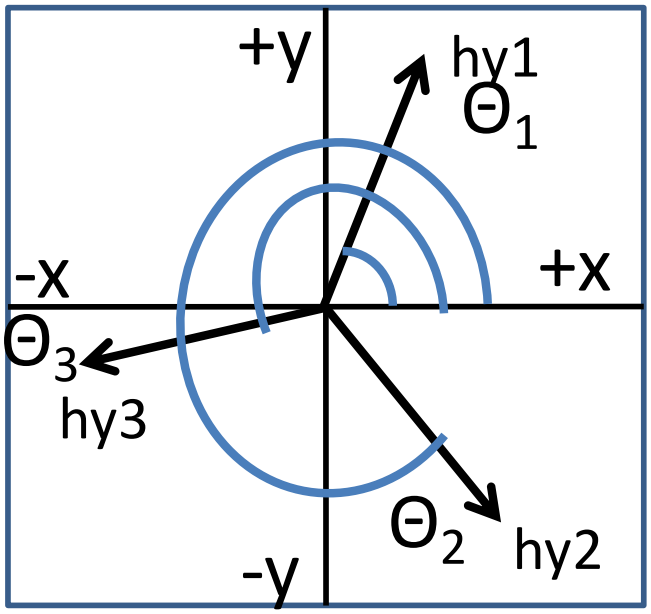
Alkines H–C≡CR

Trigonal Environment: Mixing s & 2-p

p_x and p_y can be combined with s to get three 3 equivalent hybrids at 120° to each other







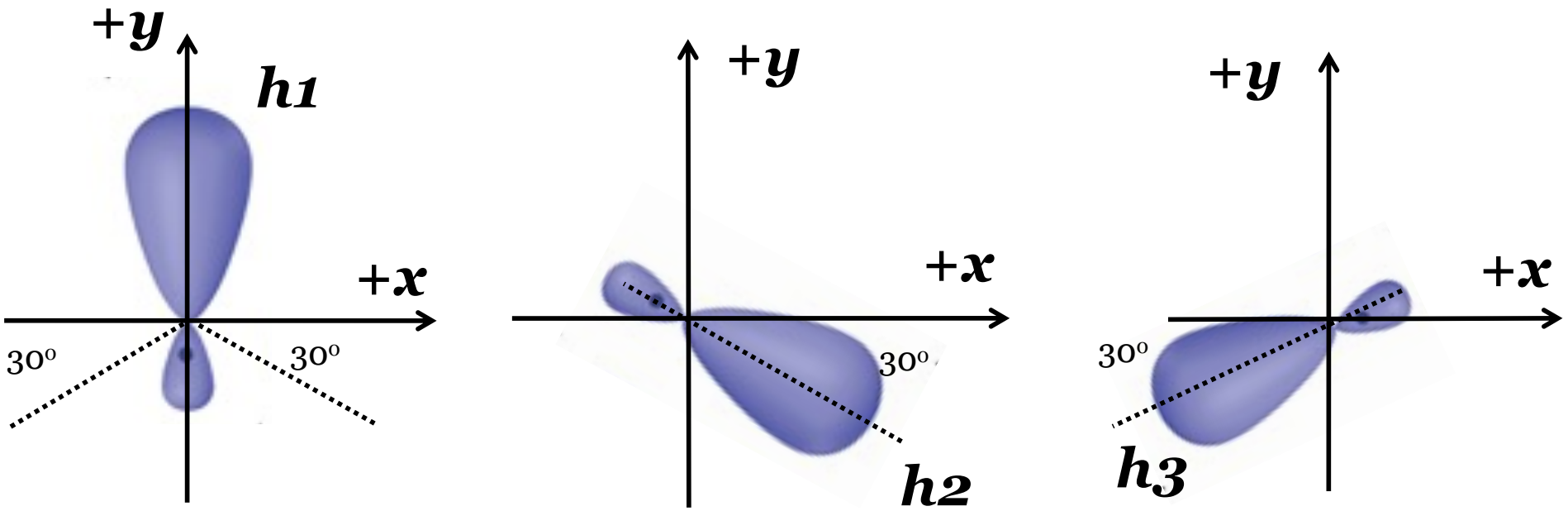
Signs of un – normalized hybrid orbitals

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

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

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

Signs of AOs for specific sp^2 hybrid orbitals (given an orientation)



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

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

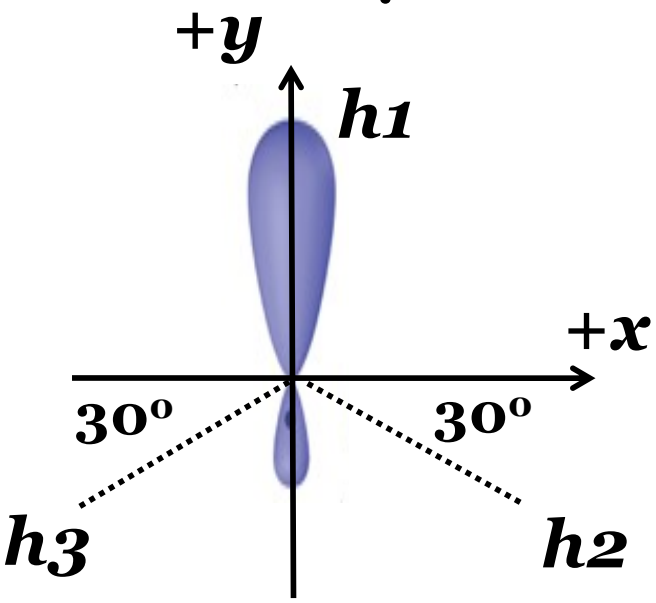
$$\varphi_{h2}^{sp^2} = c_7\psi_s + c_8\psi_{p_x} + c_9\psi_{p_y}$$

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

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

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

How to obtain coefficients for this specific geometry of sp^2?



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

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

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

$c_1^2 + c_4^2 + c_7^2 = 1$ (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*

$$c_1c_4 + c_2c_5 + c_3c_6 = 0$$

$$c_4c_7 + c_5c_8 + c_6c_9 = 0$$

$$c_7c_1 + c_8c_2 + c_9c_3 = 0$$

Each φ is *normalized*

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

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

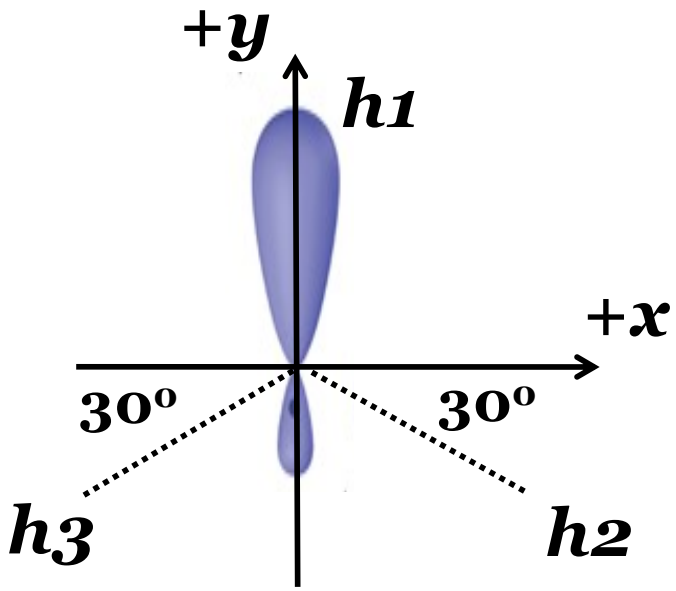
$$c_7^2 + c_8^2 + c_9^2 = 1$$

P_x and P_y Coeffs.

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

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

Signs and coefficients for these particular sp^2 hybrids

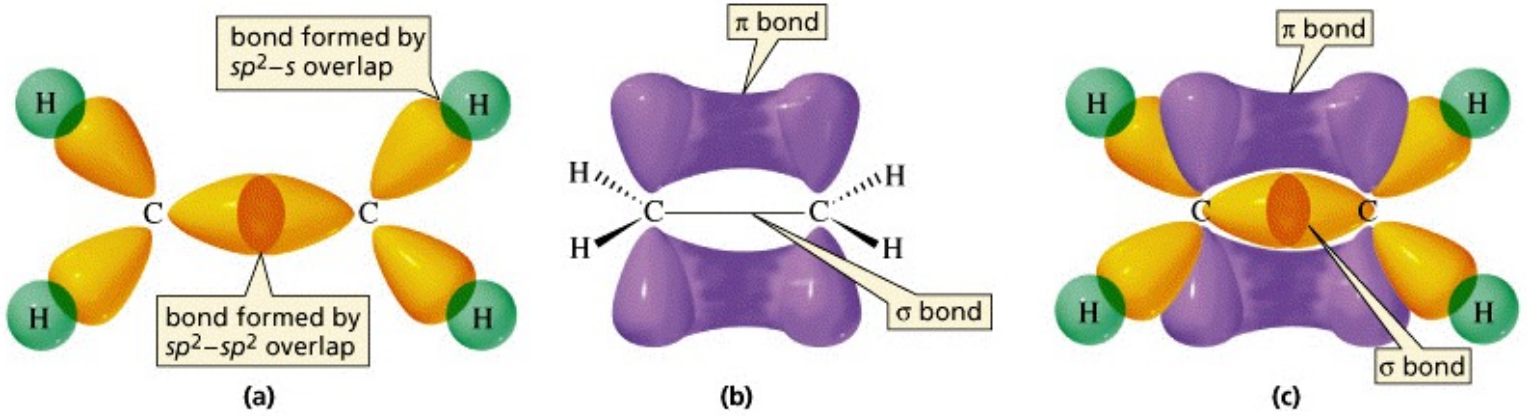


$$\varphi_{h1}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + 0.\psi_{p_x} + \sqrt{\frac{2}{3}}\psi_{p_y}$$

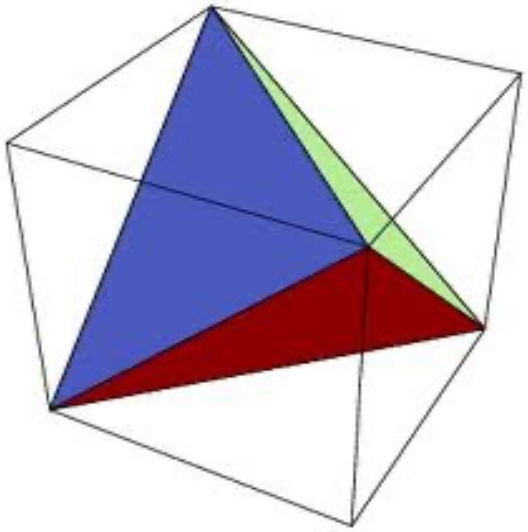
$$\varphi_{h2}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

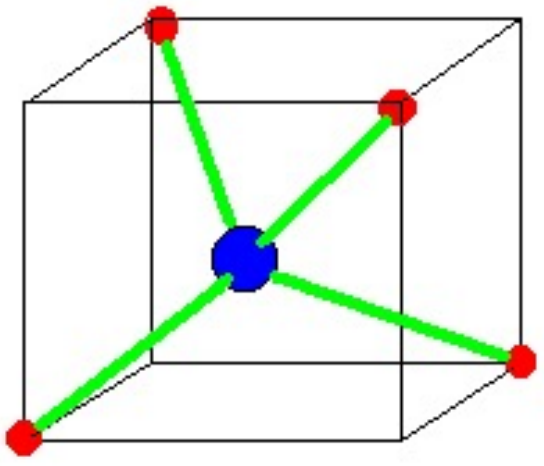
$$\varphi_{h3}^{sp^2} = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y}$$

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



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





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

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

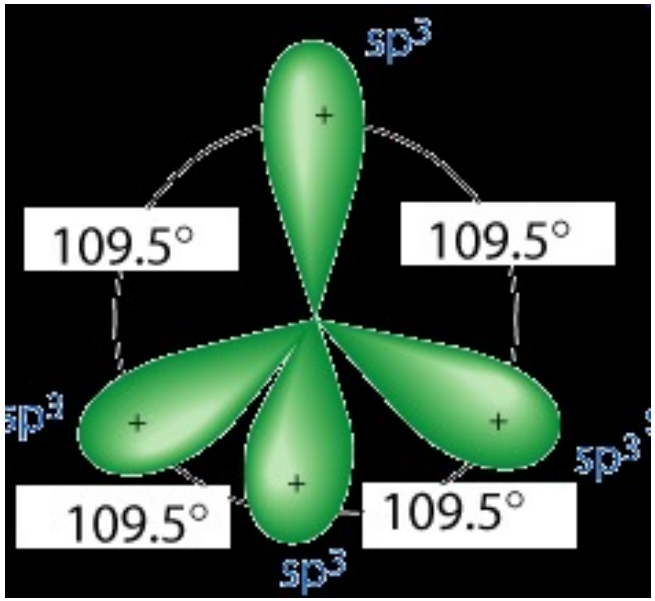
$$\varphi_{h2}^{sp^3} = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

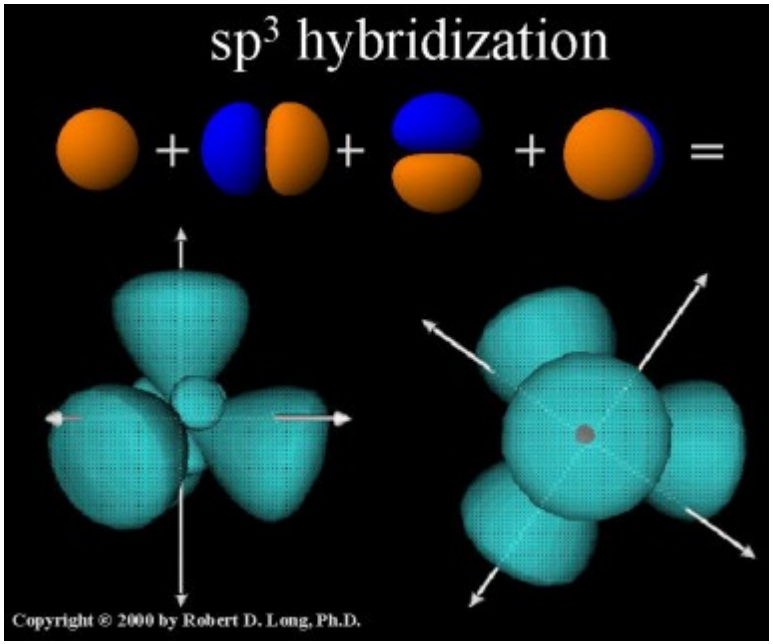
$$\varphi_{h4}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

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?



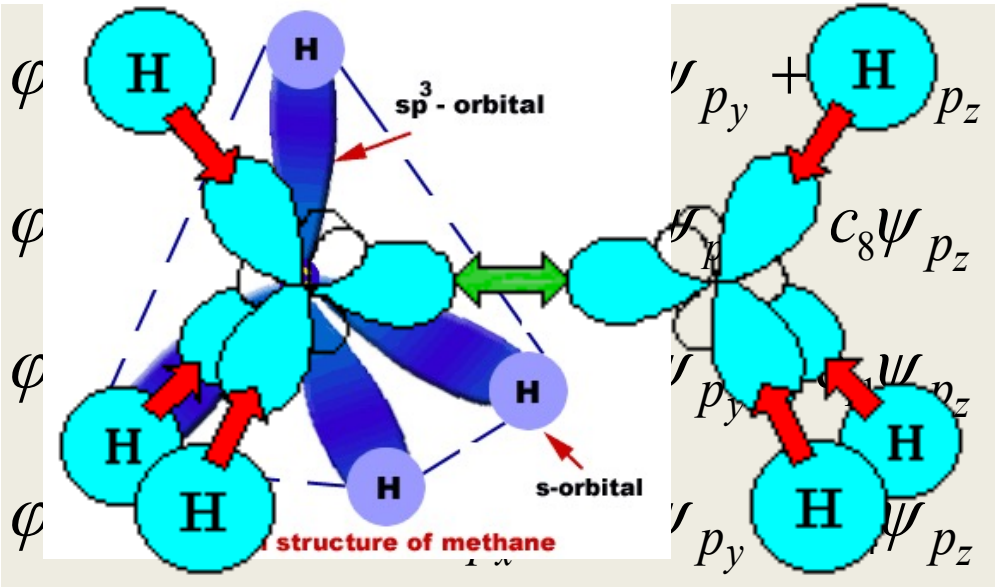


$$\varphi_{h1} = \frac{1}{2}\psi_s + 0.\psi_{p_x} + 0.\psi_{p_y} + \frac{\sqrt{3}}{2}\psi_{p_z}$$

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

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

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



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

angle between two vectors

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

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

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

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

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

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

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

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

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

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

How to get angle between hybrids?

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

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

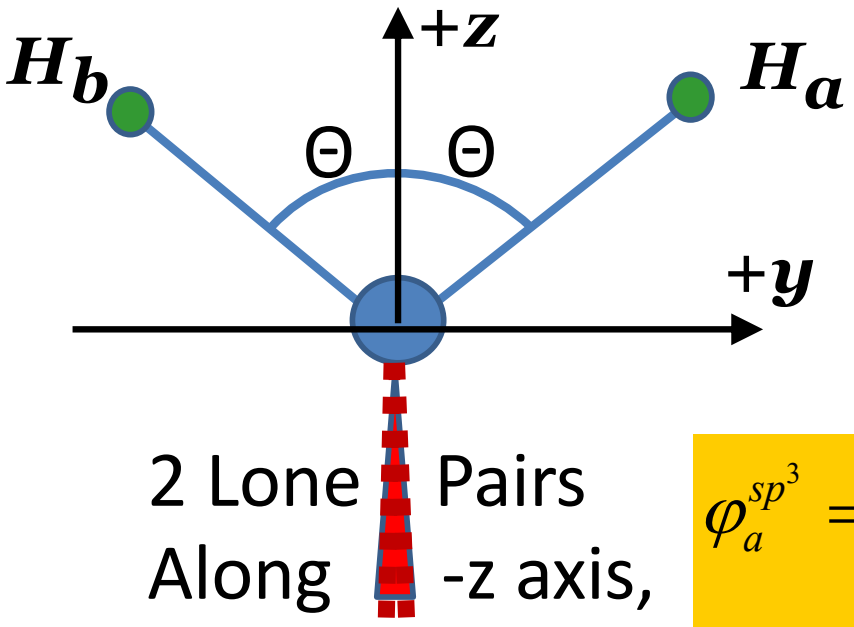
$$\overrightarrow{\varphi_{h3}} \equiv -\frac{1}{\sqrt{6}}\psi_{p_x} + \frac{1}{\sqrt{2}}\psi_{p_y} - \frac{1}{2\sqrt{3}}\psi_{p_z}$$

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

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

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

Non-equivalent Hybrid Orbitals: H_2O



H—O—H angle (2Θ = 104.5)

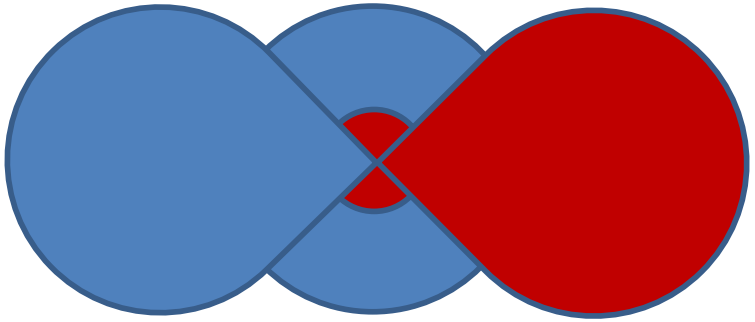
2 H atoms along +z, in yz plane
2 Lone pair of electrons in xz plane (-z)

2 Lone Pairs Along -z axis, In the xz plane)

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

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

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

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

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

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

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

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

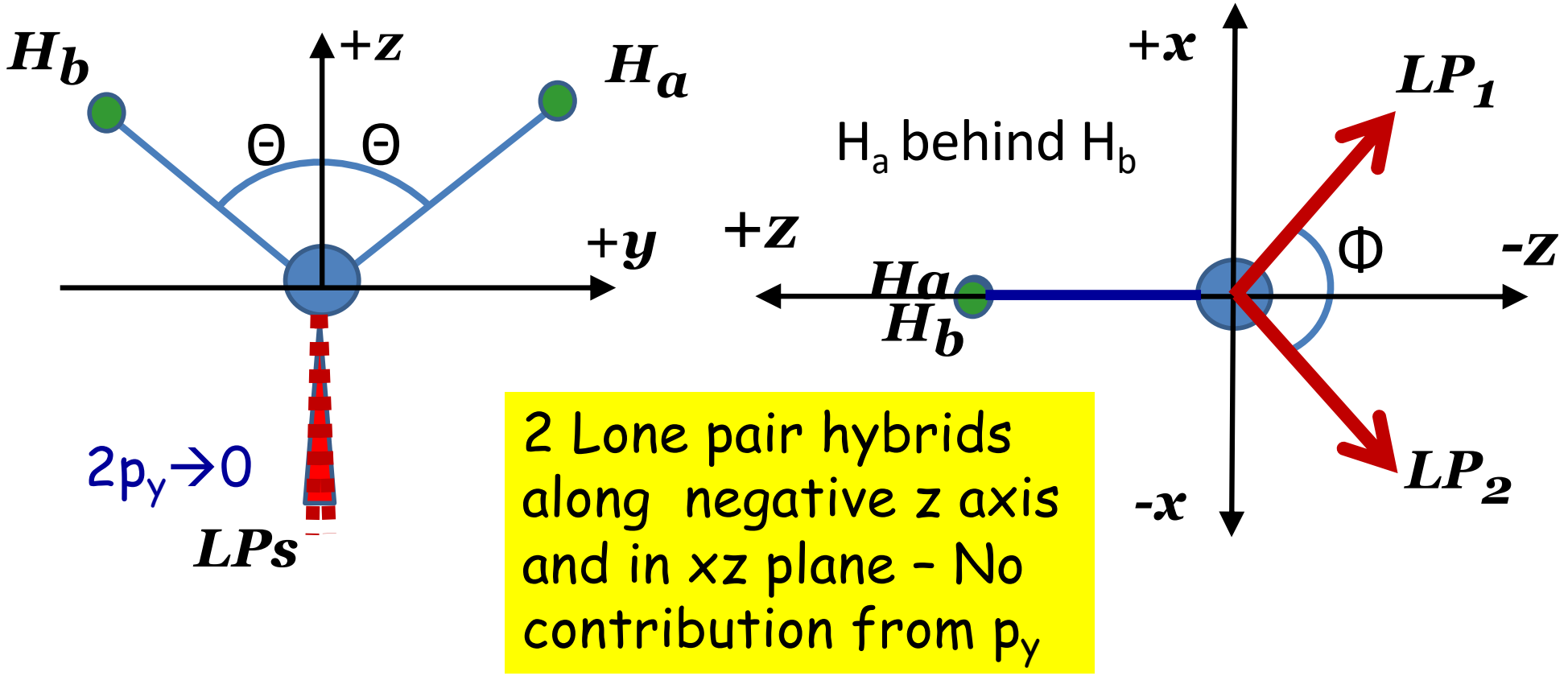
% P character: $(0.55)^2+(0.71)^2=0.80$ (80%)
% S character = $(-0.45)^2 = 0.2$ (20%)
➔ more like SP4 , rather than SP3

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

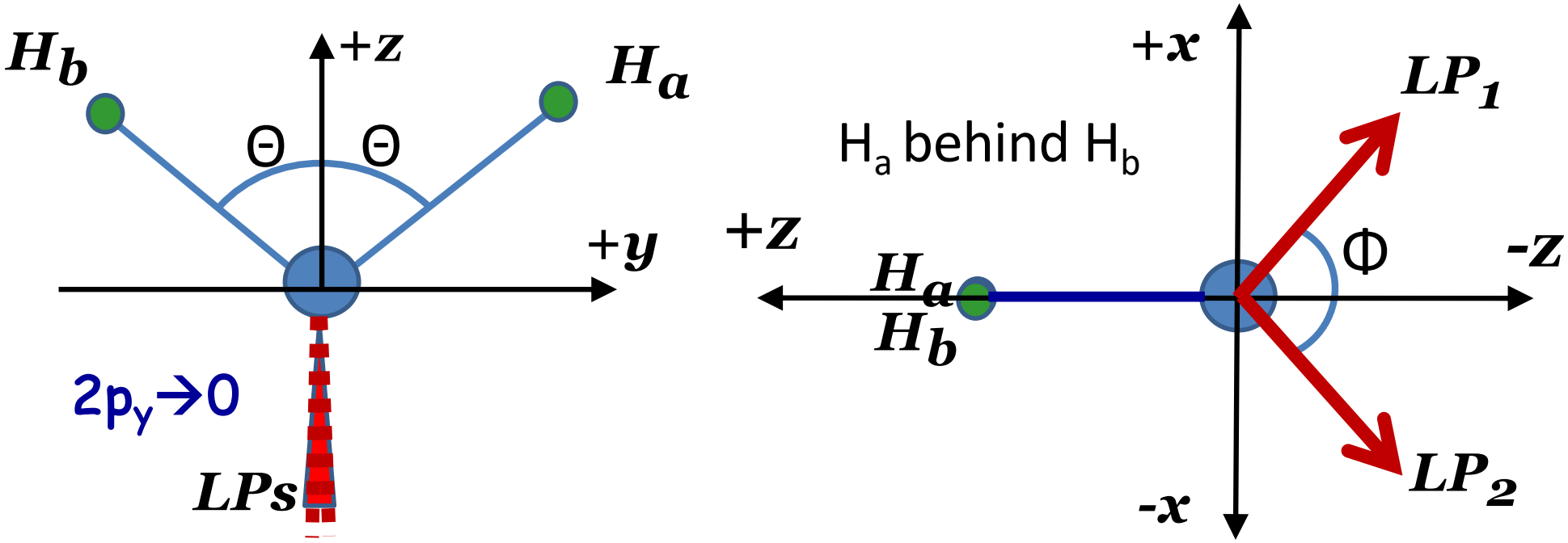
$$\varphi_{lp1}^{sp^3} = d_1.\psi_{2p_z} + 0.\psi_{2p_y} + d_3.\psi_{2s} + d_4.\psi_{2p_x}$$

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

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



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

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

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

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:

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

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

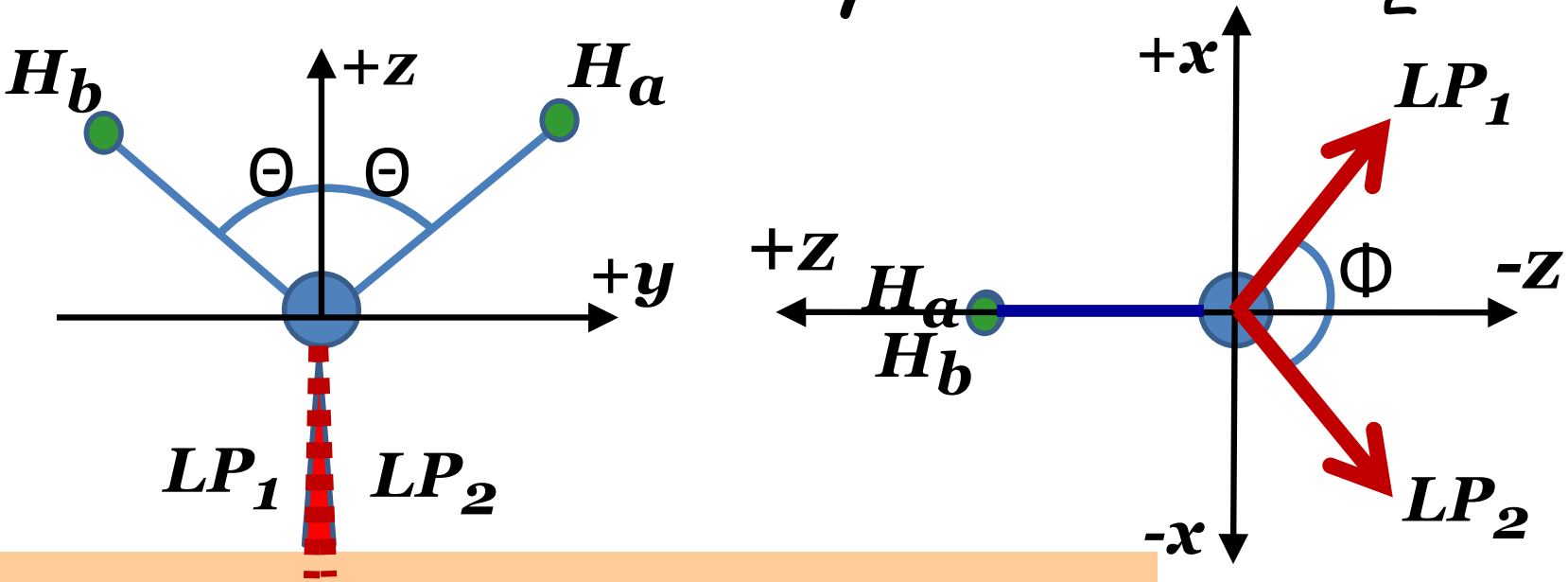
For $2p_z$ $\quad d_1^2 + d_1^2 + (0.55)^2 + (0.55)^2 = 1 \rightarrow d_1 = \pm 0.45$

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



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

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

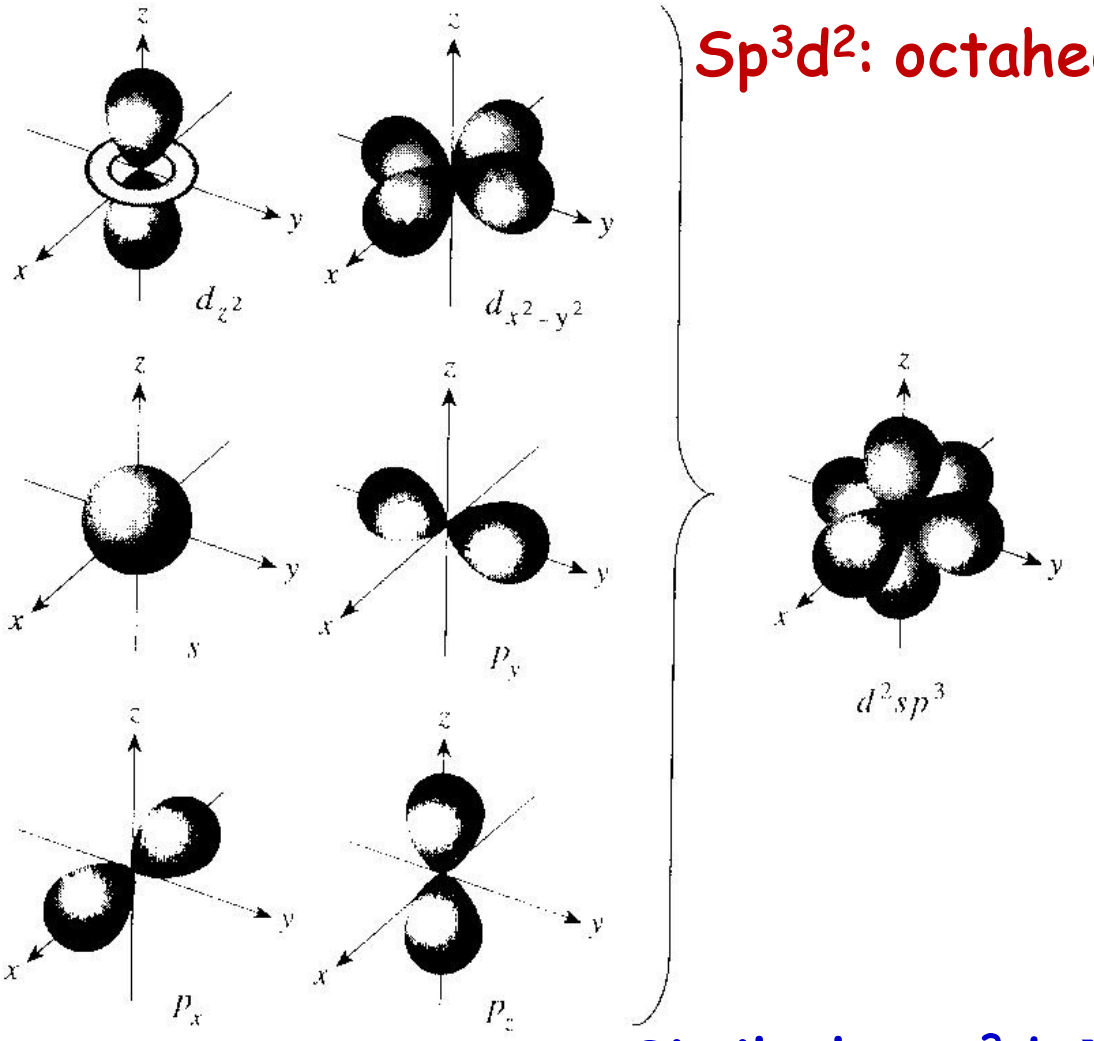
S➔$(0.55)^2$➔30%
P➔100-30➔70%

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

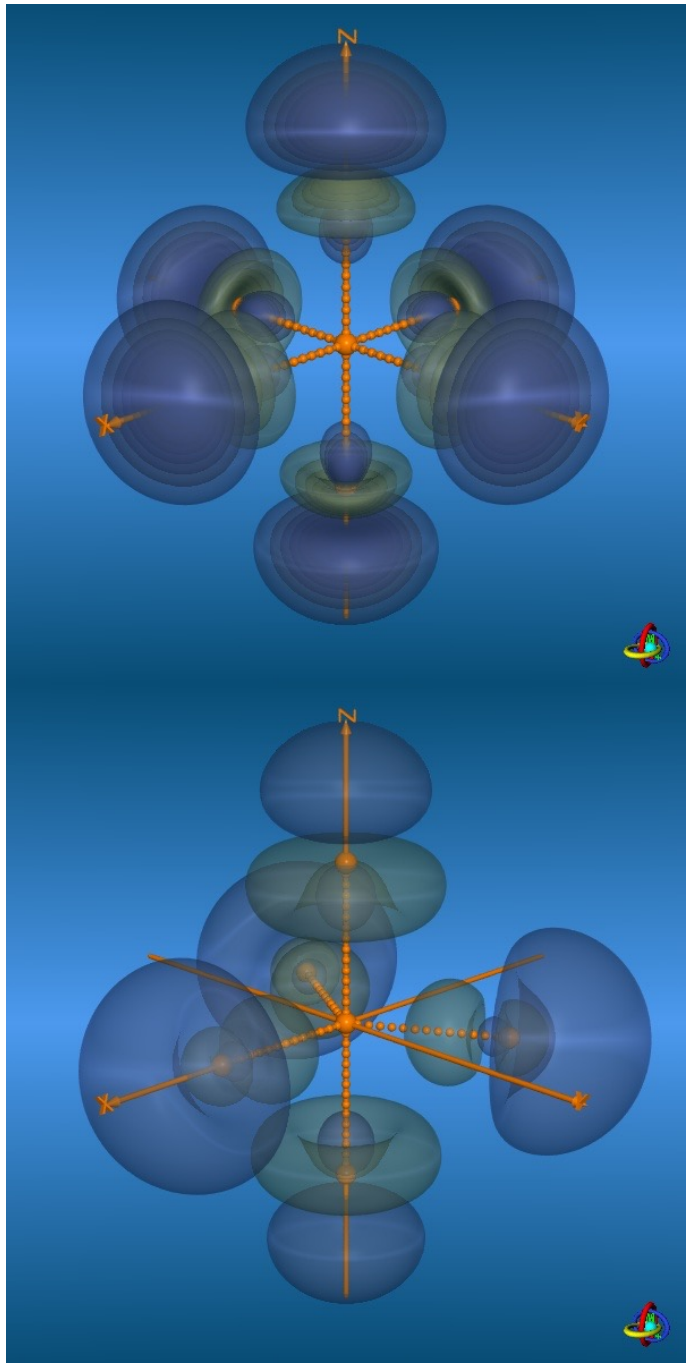
$$\varphi_{b}^{sp^3} = 0.55.\psi_{2p_z} - 0.71.\psi_{2p_y} - 0.45.\psi_{2s} + 0.\psi_{2p_x}$$

S➔ 20%
P➔ 80%

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

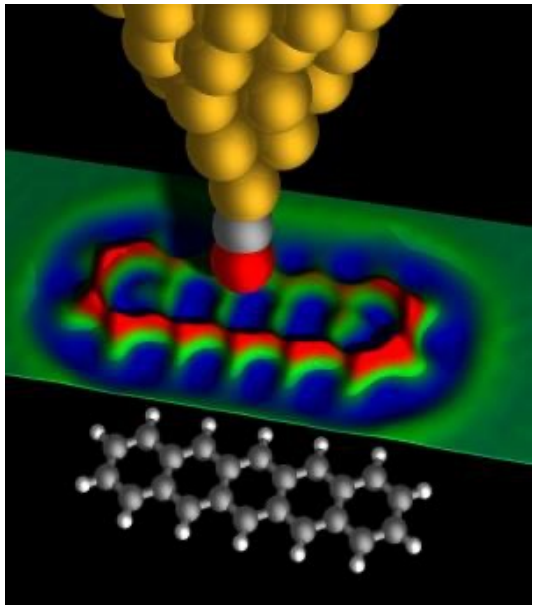


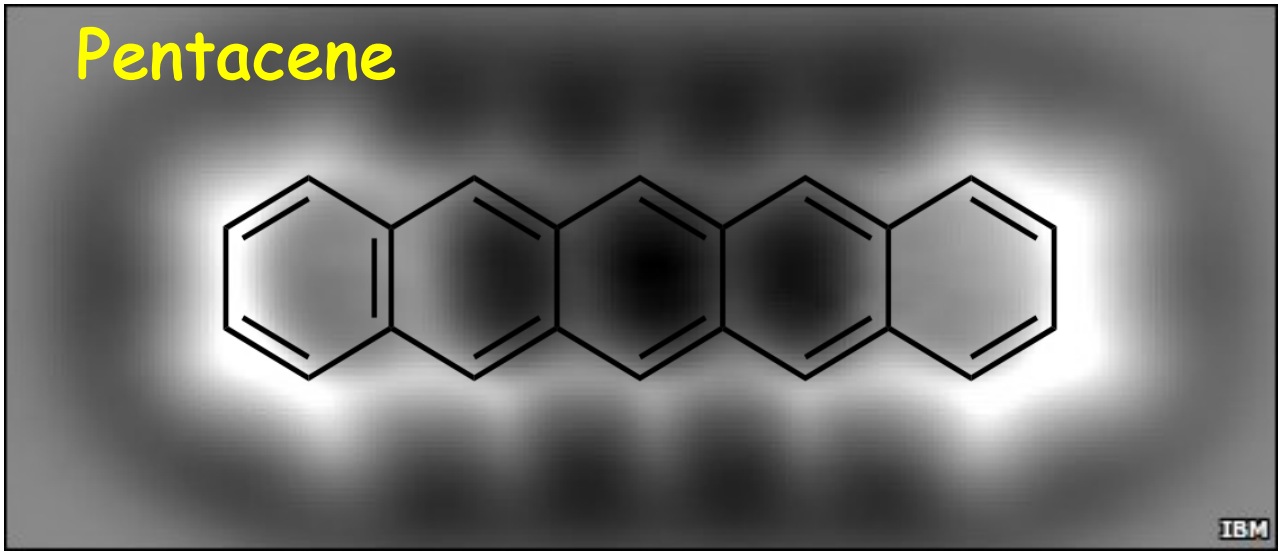
Sp^3d^2: octahedral

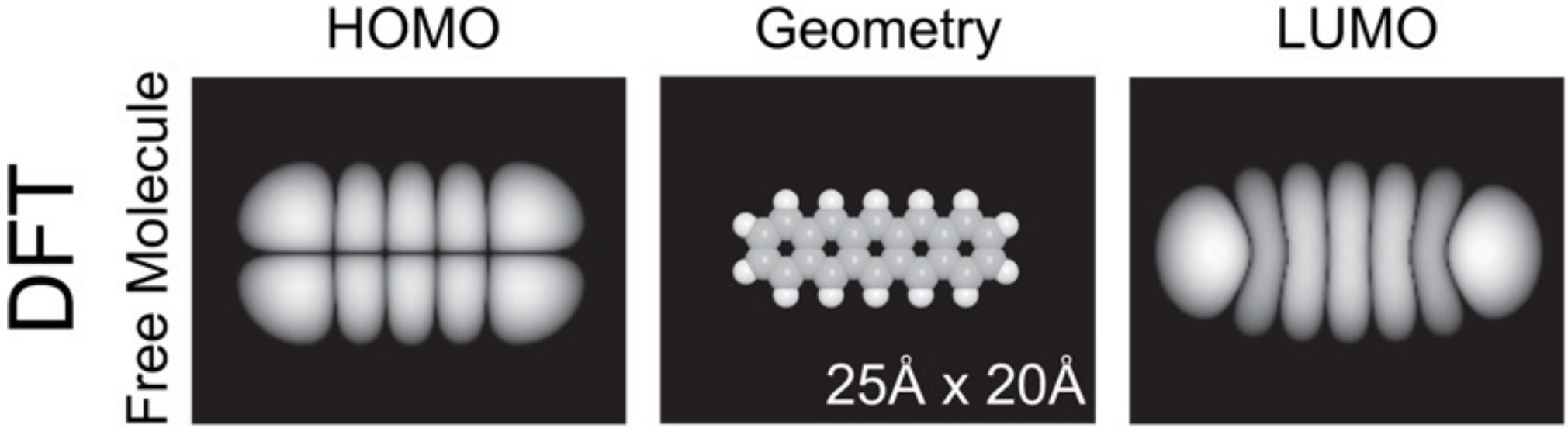


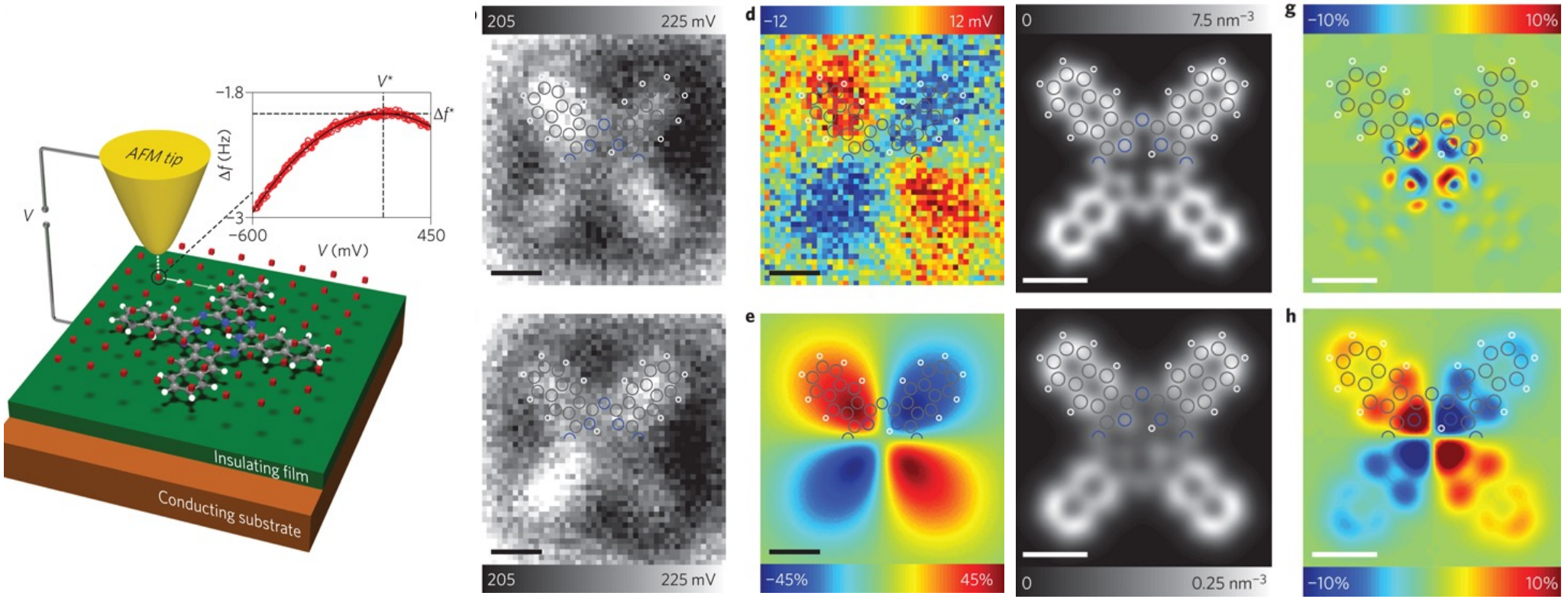
Similarly, sp^3d → trigonal bipyramidal

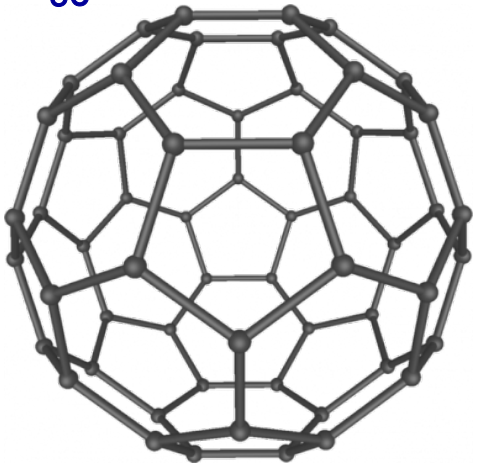
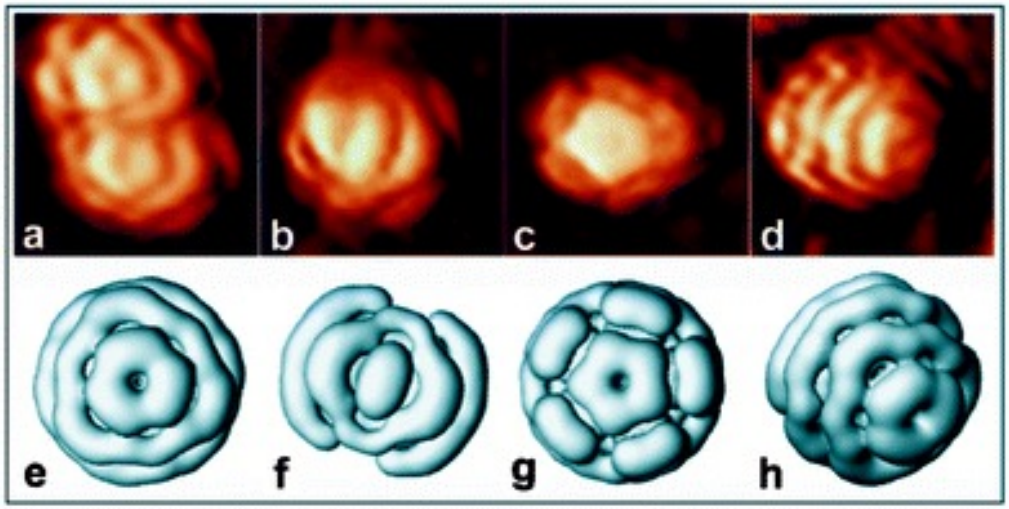
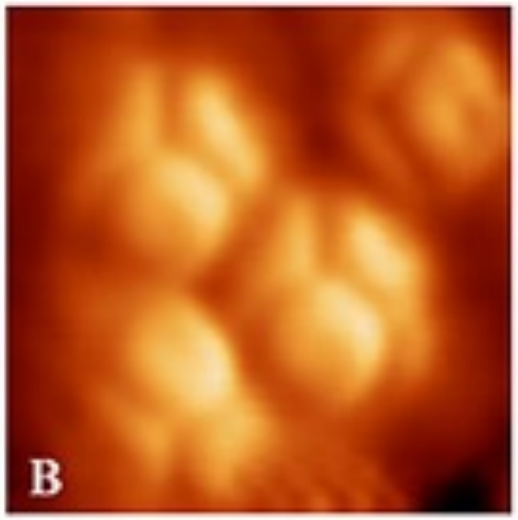
Experimental mapping of electron density (or MO) for individual molecules









Collaboration of engineers and scientists has led to such fantastic discoveries

C_{60}: Fullerene