(e) sp hybridization and Hybrid orbitals

- Just LCAO
- LCAO : using s and p from same atom plus AOs from other atoms and do the matrix calculation

Key idea

(24) Some cases have strong mixings of s and p from the same atom

(this is a result of QM LCAO calculation)

and these mixed (hybrid) orbitals form bonds with AOs of other atoms

- BeH_2 exist (exp'tal fact). It is a linear molecule H-Be-H.

Be: $1s^2 \underbrace{2s^2}$ all full! But $2s$ — $\overline{}$ $\overline{}_{2p_z}$ $\overline{}_{2p_x}$ $\overline{}_{2p_y}$ $\downarrow\uparrow$ not much different

- 

$2s \; \underline{\uparrow}$ $\;\underset{2p_z}{\underline{\uparrow}}$ $\;\underset{2p_y}{\underline{}}$ $\;\underset{2p_x}{\underline{}}$

- Include Be's $2s$ and $2p_z$ AO's into LCAO consideration
- Hydrogen <u>1s</u> <u>from</u> "left" <u>AND</u> 1s <u>from</u> "Right"

$\therefore 4\times4$

So, schematically

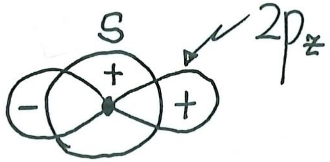
LCAO $\Rightarrow$

$$\begin{array}{c|c:cc:c}
 & \psi_H^{(L)} & \phi_{Be,2s} & \phi_{Be,2p_z} & \psi_H^{(R)} \\
\hline
\psi_H^{(L)} & & & & \\
\hdashline
\phi_{Be,2s} & & \text{But} & & \\
\phi_{Be,2p_z} & & \text{Look Here!} & & \\
\hdashline
\psi_H^{(R)} & & & &
\end{array}$$

Solve 4×4 $\Rightarrow$ Done!

It is "legal" (mathematically) to manipulate [change basis] the <u>2x2 block</u> formed by Be's AOs

Be



$$\begin{array}{c|cc} & \phi_{Be,2s} & \phi_{Be,2p_z} \\ \hline \phi_{Be,2s} & & \\ \phi_{Be,2p_z} & & \end{array}$$

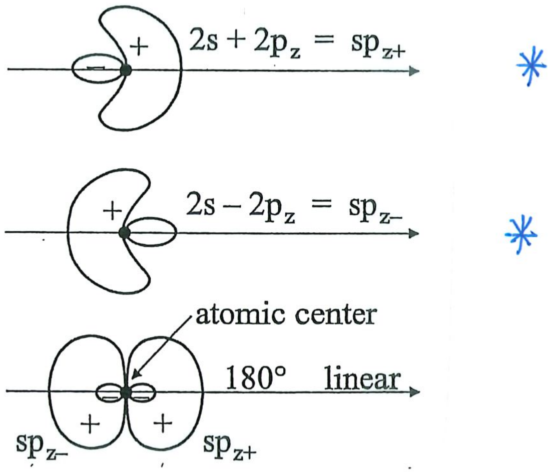
Advantageous to form linear combinations: ["two in two out"]

$$\psi^{(Be)}_{sp\,hybrid\,1} \sim \psi_{Be,2s} + \psi_{Be,2p_z}$$

$$\psi^{(Be)}_{sp\,hybrid\,2} \sim \psi_{Be,2s} - \psi_{Be,2p_z}$$

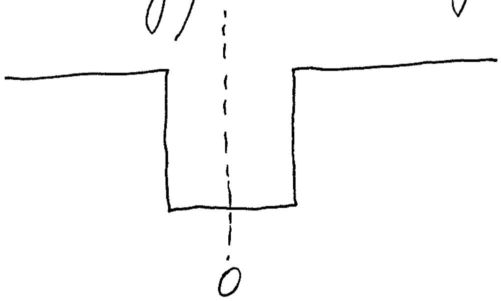
same atom

sp hybridization

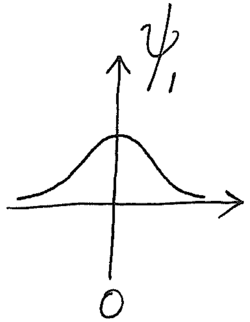


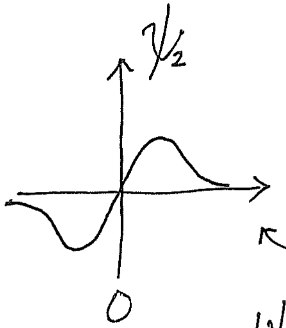
* Besides pointing at different directions, the two hybrid orbitals are equivalent. Highly directional, for stronger bonds with H-1s AO's on both sides

Analogy : 1D finite well



Ground state (like s)





1st excited state (like p)

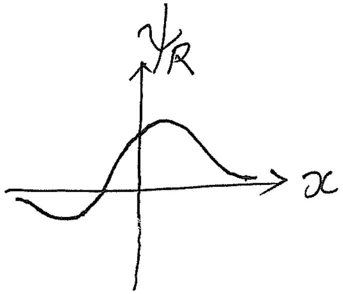
analogous to hybrid orbitals

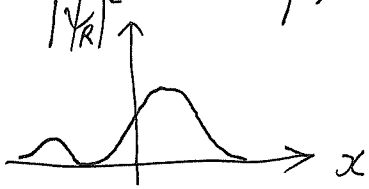
$$\psi_R \propto \psi_1 + \psi_2$$

$[\text{like } \psi_s + \psi_p]$

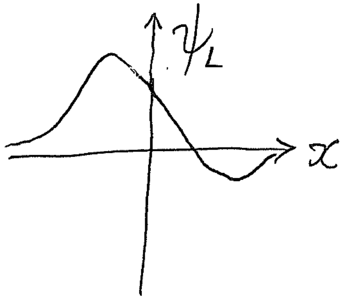
$$\psi_L \propto \psi_1 - \psi_2$$

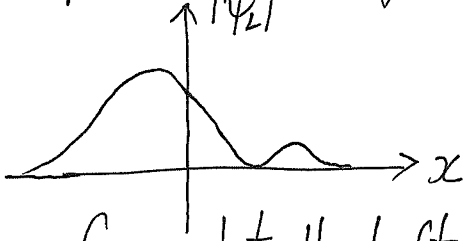
$[\text{like } \psi_s - \psi_p]$





focused to the Right

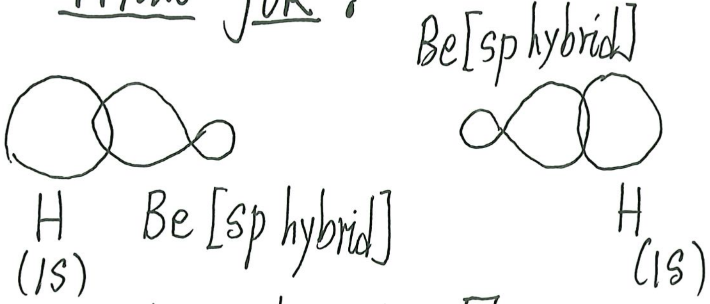




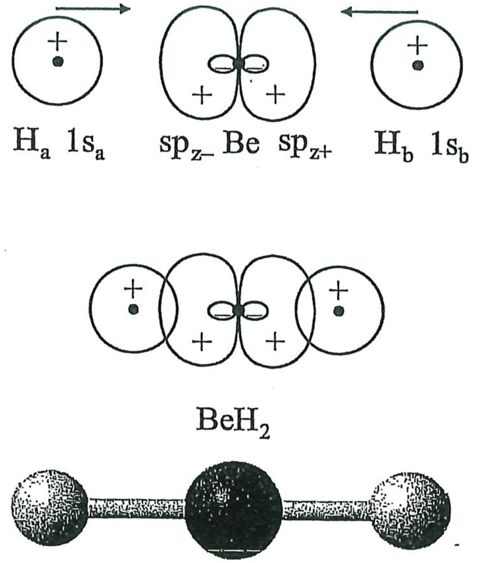
focused to the Left

To prepare for forming bonds with atoms in the right (using ψ_R) and in the left (using ψ_L)

What for?



[Good overlap, strong bond]



[energy is lowered]

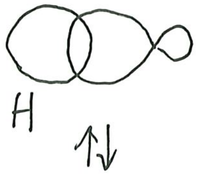
Mathematically speaking

after changing basis to $\psi^{(Be)}_{sp\#1}$, $\psi^{(Be)}_{sp\#2}$

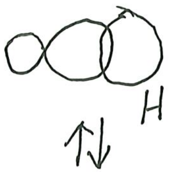
4×4 matrix becomes

$$\begin{array}{c|cc|cc}
 & \psi^{(L)}_{H} & \psi^{(Be)}_{sp\#2} & \psi^{(Be)}_{sp\#1} & \psi^{(R)}_{H} \\
\hline
\psi^{(L)}_{H} & \varepsilon^{(H)}_{1s} & \Delta & \approx 0 & \approx 0 \\
\psi^{(Be)}_{sp\#2} & \Delta^{*} & \varepsilon^{(Be)}_{hybrid} & \approx 0 & \approx 0 \\
\hline
\psi^{(Be)}_{sp\#1} & \approx 0 & \approx 0 & \varepsilon^{(Be)}_{hybrid} & \Delta^{*} \\
\psi^{(R)}_{H} & \approx 0 & \approx 0 & \Delta & \varepsilon^{(H)}_{1s}
\end{array}$$

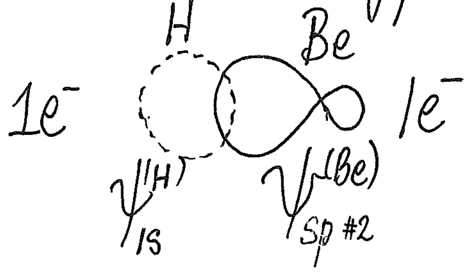
2x2 block (upper)



2x2 block (lower)

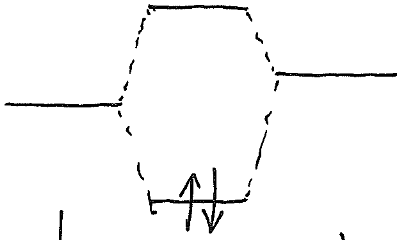


Gain Energy by forming bonds (BeH_2)



$$\begin{array}{c} \\ \psi_H^{(L)} \\ \psi_{sp\#2}^{(Be)} \end{array} \begin{array}{cc} \psi_H^{(L)} & \psi_{sp\#2}^{(Be)} \\ \left(\begin{array}{c} \varepsilon_{1s}^{(H)} \\ \Delta^* \end{array} \right. & \left. \begin{array}{c} \Delta \\ \varepsilon_{hybrid}^{(Be)} \end{array} \right) \end{array}$$

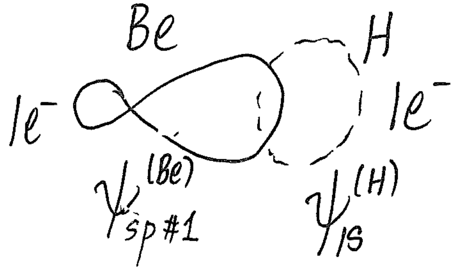
($|\Delta|$ becomes bigger)



stronger pushing lowers energy

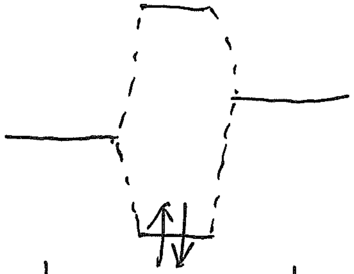
H — Be ····· H

this bond



$$\begin{pmatrix} \varepsilon_{hybrid}^{(Be)} & \Delta^* \\ \Delta & \varepsilon_{1s}^{(H)} \end{pmatrix}$$

($|\Delta|$ becomes bigger)



stronger pushing lowers energy

H ····· Be — H

this bond

Deeper: "Hybridization" is just a way to describe the wavefunction of Be, it is not an event

- Let's see. 2s —•— —•— 2p (Be) > 2 electrons (in $\underbrace{2s}_{\psi_s}$ & $\underbrace{2p}_{\psi_p}$)

$\uparrow$ Be atomic orbitals

$$\boxed{\text{"One electron in } \psi_s \text{ and one electron in } \psi_p\text{"}}$$

This is the physical situation (that we want to describe)

Description 1: Easy! 2 electrons in two states

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_s(1) & \psi_p(1) \\ \psi_s(2) & \psi_p(2) \end{vmatrix} \quad (25)$$

satisfies anti-symmetric requirement

[in terms of atomic orbitals ψ_s and ψ_p (same atom)]

Description 2 : Introduce "Hybrid orbitals"

$$\psi_A = \frac{1}{\sqrt{2}}(\psi_s - \psi_p) \quad ; \quad \psi_B = \frac{1}{\sqrt{2}}(\psi_s + \psi_p) \qquad (26)$$

[just two single-electron states mix & form two other single-electron states]

▪ ψ_A , ψ_B are the sp hybrid orbitals

With 2 electrons, we could as well say that "one electron in ψ_A and one electron in ψ_B"

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_A(1) & \psi_B(1) \\ \psi_A(2) & \psi_B(2) \end{vmatrix} \qquad (27)$$

[in terms of hybrid orbitals]

$\Psi(1,2)$ vs $\Phi(1,2)$? Are they different?

$$\Phi(1,2) = \frac{1}{\sqrt{2}}\left[\psi_A(1)\,\psi_B(2) - \psi_B(1)\,\psi_A(2)\right]$$

$$= \frac{1}{\sqrt{2}}\,\frac{1}{2}\Big[\big(\psi_s(1)-\psi_p(1)\big)\big(\psi_s(2)+\psi_p(2)\big) - \big(\psi_s(1)+\psi_p(1)\big)\big(\psi_s(2)-\psi_p(2)\big)\Big] \quad (\text{using } (24))$$

$$= \frac{1}{\sqrt{2}}\,\frac{1}{2}\Big[\cancel{\psi_s(1)\,\psi_s(2)} + \psi_s(1)\,\psi_p(2) - \psi_p(1)\,\psi_s(2) - \cancel{\psi_p(1)\,\psi_p(2)}$$
$$- \cancel{\psi_s(1)\,\psi_s(2)} + \psi_s(1)\,\psi_p(2) - \psi_p(1)\,\psi_s(2) + \cancel{\psi_s(1)\,\psi_p(2)}\Big]$$

$$= \frac{1}{\sqrt{2}}\left[\psi_s(1)\,\psi_p(2) - \psi_p(1)\,\psi_s(2)\right] = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_s(1) & \psi_p(1)\\ \psi_s(2) & \psi_p(2)\end{vmatrix}$$

$$= \Psi(1,2)$$

They Describe the same wavefunction!

(∴ Hybridization is nothing fancy!)

- ψ_s, ψ_p are AOs of Be atom $\Rightarrow \int \psi_{\underset{(p)}{s}}^{*}\, \psi_{\underset{(p)}{s}}\, d\tau = 1$ and $\underbrace{\int \psi_s^{*}\, \psi_p\, d\tau = 0}_{\text{orthogonal}}$

- $\psi_A = \frac{1}{\sqrt{2}}\psi_s + c_A \psi_p$; $\psi_B = \frac{1}{\sqrt{2}}\psi_s + c_B \psi_p$ (Find c_A, c_B systematically)

[Why $\frac{1}{\sqrt{2}}$ in front of ψ_s? The s-orbital will <u>NOT</u> bias ψ_A OR ψ_B]

Require ψ_A to be normalized $\Rightarrow \int \psi_A^{*}\psi_A\, d\tau = \frac{1}{2}\int \psi_s^{*}\psi_s\, d\tau + c_A^2 \int \psi_p^{*}\psi_p\, d\tau = 1$

$$\Rightarrow c_A = \frac{1}{\sqrt{2}}$$

$$\therefore \boxed{\psi_A = \frac{1}{\sqrt{2}}(\psi_s + \psi_p)} \quad (28a)$$

Require ψ_B and ψ_A be $\underset{\text{(mathematically)}}{\underline{\text{orthogonal}}}$ $\Rightarrow \int \psi_A^{*}\psi_B\, d\tau = \frac{1}{2}\int \psi_s^{*}\psi_s\, d\tau + \frac{1}{\sqrt{2}} c_B \int \psi_p^{*}\psi_p\, d\tau = 0$

$$\Rightarrow c_B = -\frac{\sqrt{2}}{2} = -\frac{1}{\sqrt{2}}$$

$$\therefore \boxed{\psi_B = \frac{1}{\sqrt{2}}(\psi_s - \psi_p)} \quad (28b)$$

$\underset{\rightarrow \vec{V}_A}{\psi_A \sim +\psi_p}$ (point at $+\hat{z}$ direction); $\underset{\vec{V}_B \leftarrow}{\psi_B \sim -\psi_p}$ ($-\hat{z}$-direction) $\overbrace{\text{(180° apart)}}^{\text{in physical space}}$

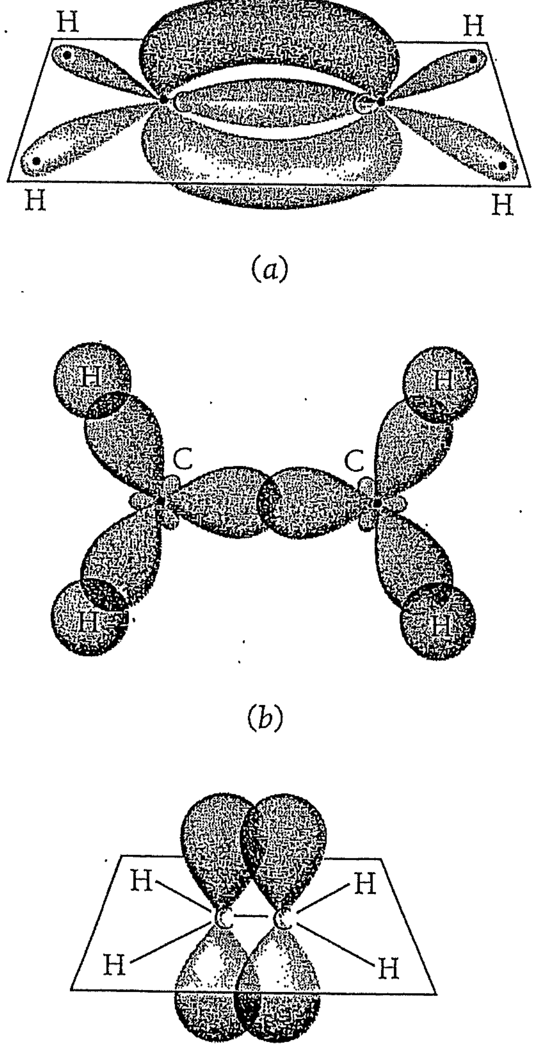
$$\boxed{\vec{V}_A \cdot \vec{V}_B = -1}$$

The deeper description and approach of getting the hybrid orbitals (sp in this case) are applicable to sp^2 and sp^3 hybridization

- s won't bias any hybrid orbital
- Hybrid orbitals are themselves <u>normalized</u> and mutually <u>orthogonal</u>
- spread out in space for bonding with other atoms.

(f) C_2H_4 (ethylene) and sp^2 hybridization

double (one σ and one π) bond



(a)

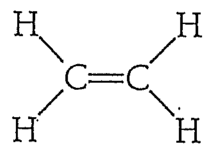
(b)

(c)

Top View

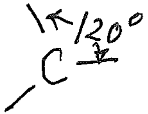
(a) The ethylene (C_2H_4) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the sp^2 hybrid orbitals that form σ bonds between the C atoms and between each C atom and two H atoms. (c) Side view, showing the pure p_x orbitals that form a π bond between the C atoms.

Ethylene



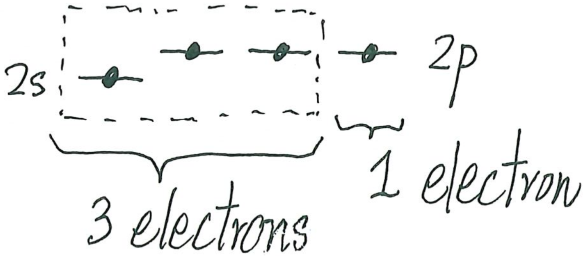
Again, highly directional

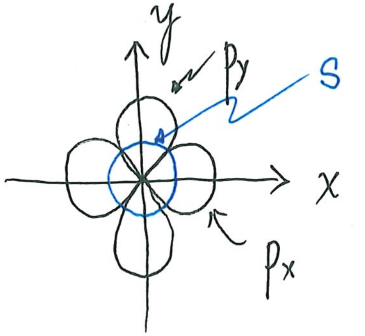
[120° between bonds.]



The two electrons in the two pure p-orbitals form a π-bond

Carbon: $[1s^2]\,2s^2\,2p^2$





$$\boxed{\psi_{2s}\,,\ \psi_{2p_x}\,,\ \psi_{2p_y}\ \text{to form 3}\ sp^2\ \text{hybrid orbitals}}$$

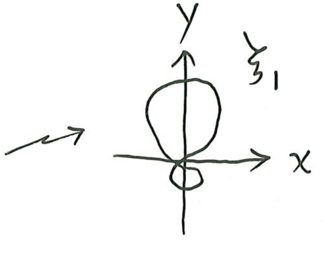
Let ξ_1, ξ_2, ξ_3 be the hybrid orbitals

$$\xi_1 = \frac{1}{\sqrt{3}}\psi_{2s} + b_1\psi_{2p_y} + 0\cdot\psi_{2p_x}$$ [OK to put ξ_1 in $+\hat{y}$ direction, still general]

$$\xi_2 = \frac{1}{\sqrt{3}}\psi_{2s} + b_2\psi_{2p_y} + c_2\psi_{2p_x}$$

$$\xi_3 = \frac{1}{\sqrt{3}}\psi_{2s} + b_3\psi_{2p_y} + c_3\psi_{2p_x}$$

ξ_1 normalized $\Rightarrow b_1 = \sqrt{\frac{2}{3}}$ $\quad\therefore$ $\boxed{\xi_1 = \sqrt{\frac{1}{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\psi_{2p_y}}$ $\longrightarrow$



ξ_2 orthogonal to ξ_1 $\Rightarrow b_2 = -\sqrt{\frac{1}{6}}$

ξ_2 itself normalized $\Rightarrow c_2 = \sqrt{\frac{1}{2}}$ $\quad\therefore$ $\boxed{\xi_2 = \sqrt{\frac{1}{3}}\psi_{2s} - \sqrt{\frac{1}{6}}\psi_{2p_y} + \sqrt{\frac{1}{2}}\psi_{2p_x}}$ (29)

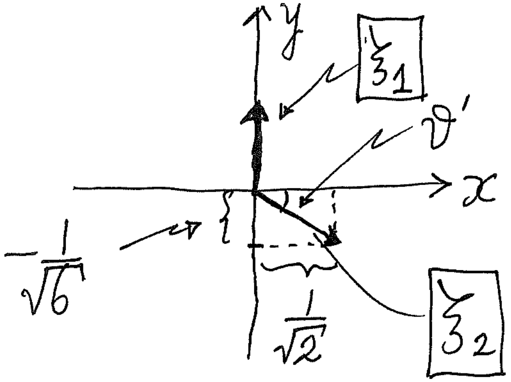
Which direction does ξ_2 point at?

Lazy way (works)

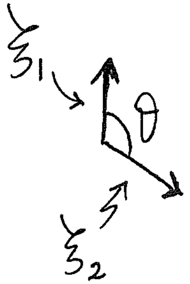
$$\xi_1 = \underbrace{\frac{1}{\sqrt{3}}\psi_{2s}}_{\text{no direction}} + \sqrt{\frac{2}{3}}\,\underbrace{\psi_{2p_y}}$$

like a vector in $\hat{y}$-direction

$$\xi_2 = \underbrace{\frac{1}{\sqrt{3}}\psi_{2s}}_{\text{no direction}} - \frac{1}{\sqrt{6}}\psi_{2p_y} + \frac{1}{\sqrt{2}}\psi_{2p_x} \sim -\frac{1}{\sqrt{6}}\,\hat{y} + \frac{1}{\sqrt{2}}\,\hat{x}$$



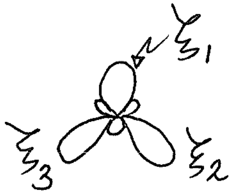
$$\tan\vartheta' = \frac{\frac{1}{\sqrt{6}}}{\frac{1}{\sqrt{2}}} = \frac{1}{\sqrt{3}} \Rightarrow \vartheta' = 30^\circ$$



$$\boxed{\theta = 90^\circ + 30^\circ = 120^\circ}$$

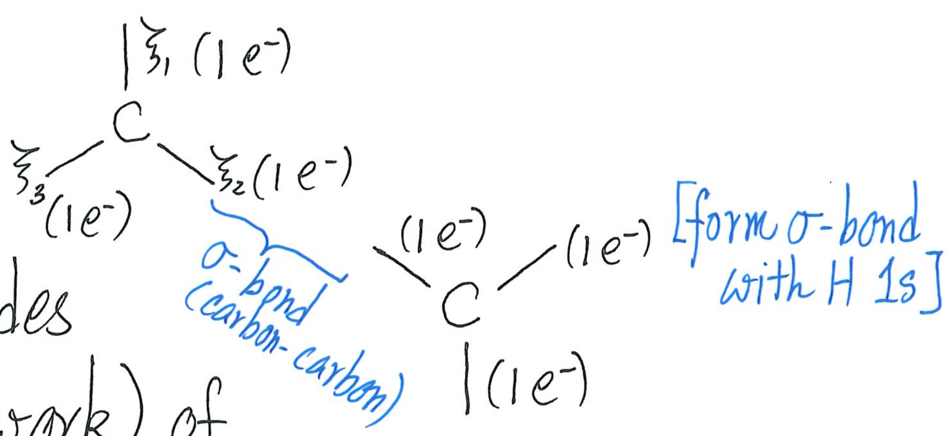
[Again, <u>QM</u> is behind directionality]

Exercise: Find ξ_3 and the direction it points at.

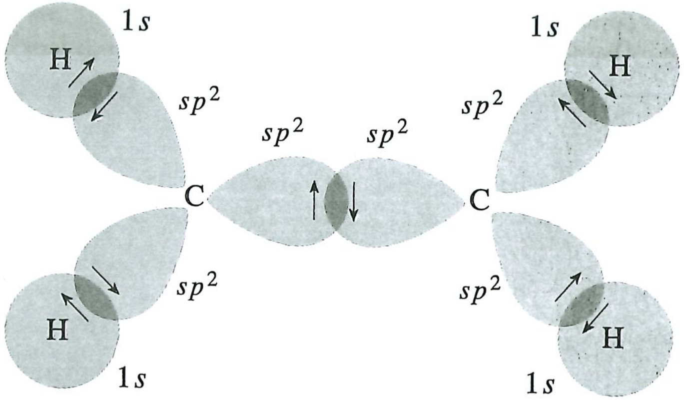


Consequences

- Plane of hybrid orbitals

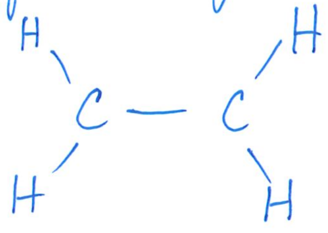


sp^2 hybridization provides the skelation (framework) of forming strong σ-bonds (direction) and dictates the structure



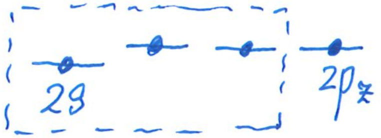
The (planar) σ-bond framework of an ethene molecule.

Rigid (strong)

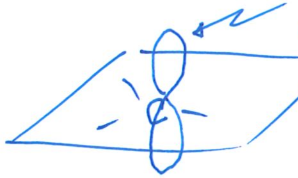


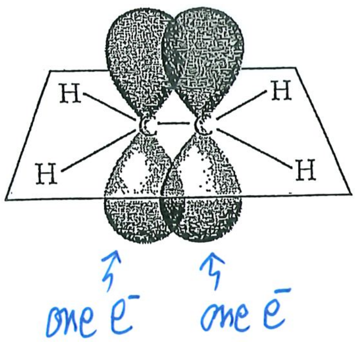
Framework

What's left?



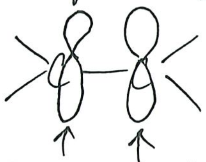
Done! (from strong framework)





Quick QM thinking on π-bond

- After forming the strong σ-bonds skeleton



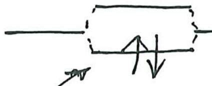
1e (2p) (left)	1e (2p) (right)

These electrons are called π electrons

$$\begin{pmatrix} \varepsilon_{2p} & \tilde{\Delta} \\ \tilde{\Delta}^* & \varepsilon_{2p} \end{pmatrix}$$

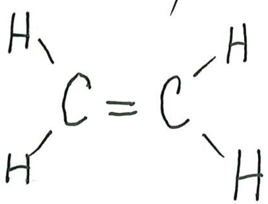
(LCAO, 2x2 matrix problem)

$$\tilde{\Delta} = \int \phi_L^* \hat{H} \phi_R \, d\tau$$



π-bond (Done!)

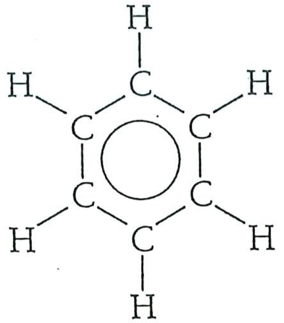
Finally



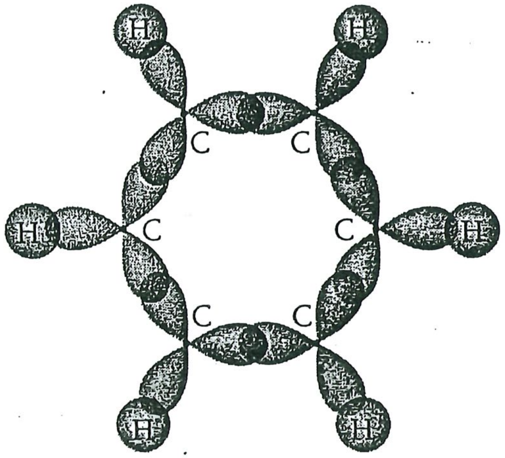
Note: $\tilde{\Delta} = \int \phi_L^* \hat{H} \phi_R \, d\tau$ can't be big (small region having non-zero integrand)

⇒ pushing is smaller ⇒ weaker than σ-bond.

(g) Benzene C_6H_6 : What is the "O" inside  ?

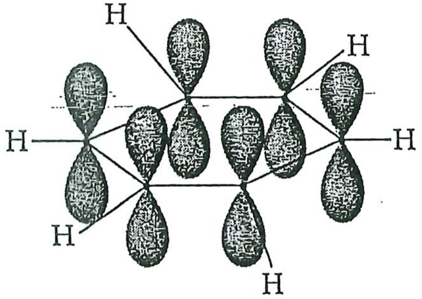


these strong bonds locked in the electrons

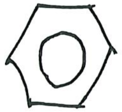


- sp^2
- σ bonds form framework 

- Each C has a $2p_z$ (perpendicular to plane) with one electron

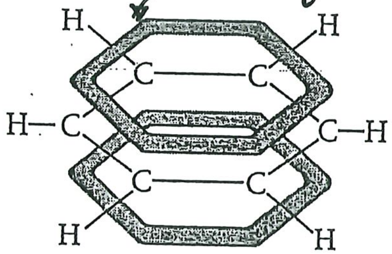


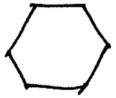
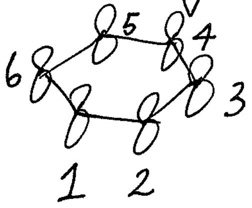
Behavior of six π-electrons?

 OR  VS 

[Quantum Mechanics Approach?]

delocalized π electrons

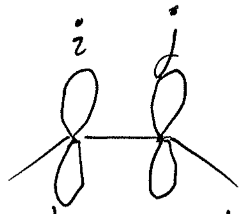


- Framework  is rigid and strong
- Q: Behavior of p_z electrons  (one electron each, six p_z electrons)

- How do they form bonds? LCAO of p_z AO's (c.f. C_2H_4 case)

Think like a physicist!! $\psi = c_1 \phi_{p_{z,1}} + c_2 \phi_{p_{z,2}} + c_3 \phi_{p_{z,3}} + c_4 \phi_{p_{z,4}} + c_5 \phi_{p_{z,5}} + c_6 \phi_{p_{z,6}}$

- Some $\hat{H}$ (don't even need to write it down explicitly)
- Formally, $\left| H_{ij} - ES_{ij} \right| = 0$ $(i, j = 1, 2, \cdots, 6)$ gives 6 values of E for 6 p_z electrons to fill in
- Practically, $S_{ii} = 1$
  $S_{ij} \approx 0$

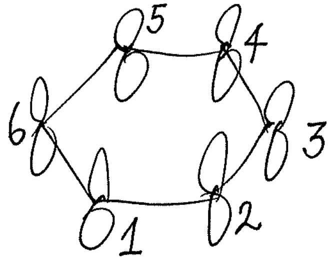


"Not much overlap"

and H_{ij} more important

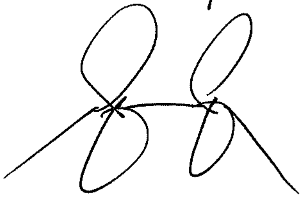
- H_{ii} is mainly governed by the atomic ε_{2p} energy

  $\Rightarrow H_{11} = H_{22} = \cdots = H_{66} = \varepsilon$ (diagonal elements)

- 

  "1"'s  interacts with $\underbrace{\text{"2" and "6" Only}}_{\text{nearest neighbors of "1"}}$

  "3", "4", "5" are $\underline{\text{farther away}}$ $\Rightarrow$ ignore H_{13}, H_{14}, H_{15}

- For two nearest neighboring  $H_{ij} = \underset{\sim}{V}$ same between two nearest neighbors

  [nearest-neighbor interaction]

∴ Need only two terms:

$$\underbrace{\underset{(\text{OR } \alpha)}{\varepsilon} \quad \text{and} \quad \underset{(\text{OR } \beta)}{V}}_{\text{in standard notations}} \quad [\beta < 0 \text{ typically}]$$

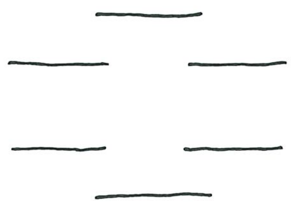
$$
\begin{array}{c|cccccc|}
 & \textcircled{1} & \textcircled{2} & \textcircled{3} & \textcircled{4} & \textcircled{5} & \textcircled{6} \\
\textcircled{1} & \varepsilon - E & V & 0 & 0 & 0 & V \\
\textcircled{2} & V & \varepsilon - E & V & 0 & 0 & 0 \\
\textcircled{3} & 0 & V & \varepsilon - E & V & 0 & 0 \\
\textcircled{4} & 0 & 0 & V & \varepsilon - E & V & 0 \\
\textcircled{5} & 0 & 0 & 0 & V & \varepsilon - E & V \\
\textcircled{6} & V & 0 & 0 & 0 & V & \varepsilon - E
\end{array} = 0
$$

gives six values of E

or written as a 6×6 matrix problem

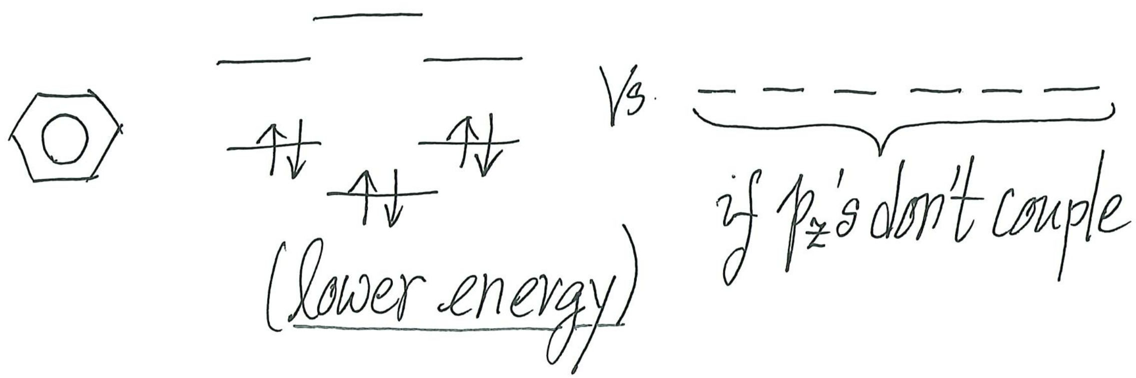
$$
\begin{pmatrix}
\varepsilon & V & 0 & 0 & 0 & V \\
V & \varepsilon & V & 0 & 0 & 0 \\
0 & V & \varepsilon & V & 0 & 0 \\
0 & 0 & V & \varepsilon & V & 0 \\
0 & 0 & 0 & V & \varepsilon & V \\
V & 0 & 0 & 0 & V & \varepsilon
\end{pmatrix}
\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix}
= E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix}
\qquad (30)
$$

- Six values of E are lined up as (there are MO's for π electrons)

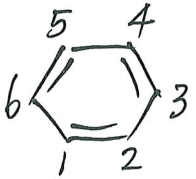


(Ex.)

- There are 6 π electrons (Pauli Principle)



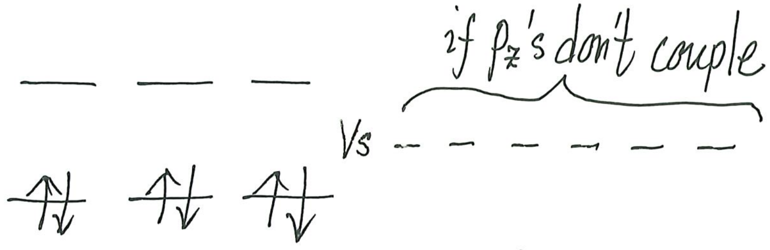
- How about



?

$$\begin{pmatrix} \varepsilon & V & 0 & 0 & 0 & 0 \\ V & \varepsilon & 0 & 0 & 0 & 0 \\ 0 & 0 & \varepsilon & V & 0 & 0 \\ 0 & 0 & V & \varepsilon & 0 & 0 \\ 0 & 0 & 0 & 0 & \varepsilon & V \\ 0 & 0 & 0 & 0 & V & \varepsilon \end{pmatrix}$$

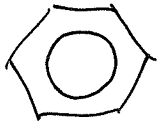
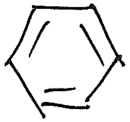
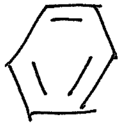
⇒ Eigenvalues



(higher energy than )

"1" only interacts with "2", etc.

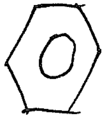
[becomes three identical 2x2 problems]

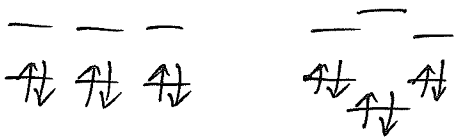
-  has a lower energy than  and 

"1" to "2" & "6", then to "3" and "5", and to "4"

⇒ **Delocalizing the electrons can lower the energy** → Benzene → Metals

Delocalizing Energy = Energy lowered by delocalizing the electrons

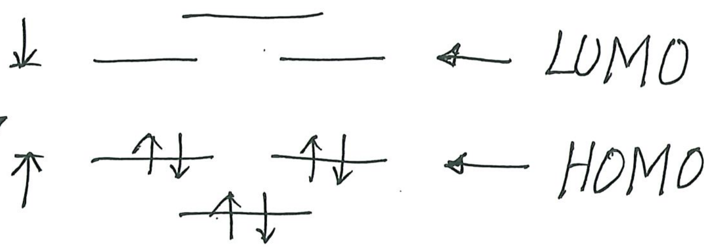
= Energy difference between  and 



- This is the Hückel Theory (1931)

Only H_{ii} (ε) (α) and nearest-neighboring H_{ij} (V) (β)

- $\underbrace{\text{LUMO}}_{\boxed{\text{lowest unoccupied molecular orbital}}} - \underbrace{\text{HOMO}}_{\boxed{\text{highest occupied molecular orbital}}}$ Difference



$\underbrace{\text{LUMO-HOMO energy difference}^{\dagger}}$ controls material's absorption/emission frequency (optical properties)

- How about butadiene?

 OR  OR something else?

- Behavior of p_z (or π) electrons in graphene, C_{60}?
- Delocalizing is key to physics of metals

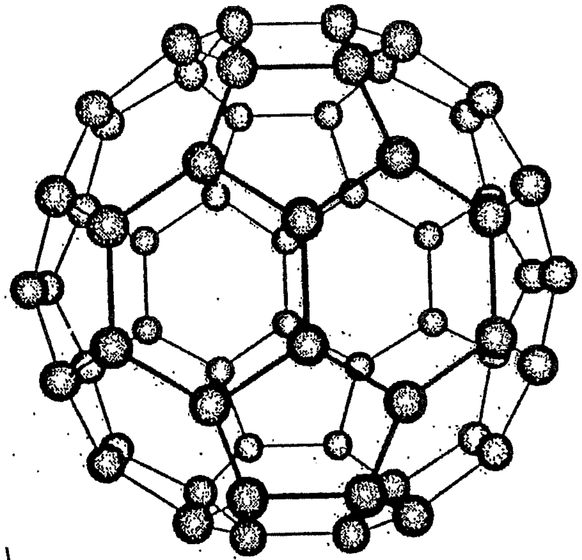
---

† The LUMO-HOMO difference becomes the band gap in insulators/semiconductors

(h) sp^2 hybridization Plus π electrons in Graphene and C_{60}

C_{60} molecule ["Bucky Ball"] [Kroto and Smalley: 1996 Nobel Chemistry Prize]

a



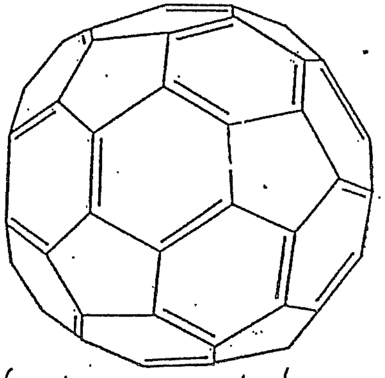
20 hexagons
12 pentagons

sp^2 hybridization
+
π electrons

diameter ~ 7 Å

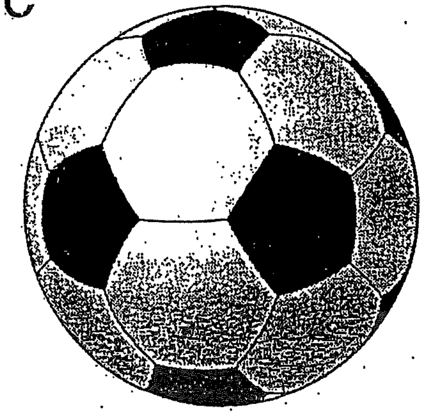
Formally, a
Truncated
Iscosohedron
↑
(二十面體)
(twenty plane faces)

b Schematic



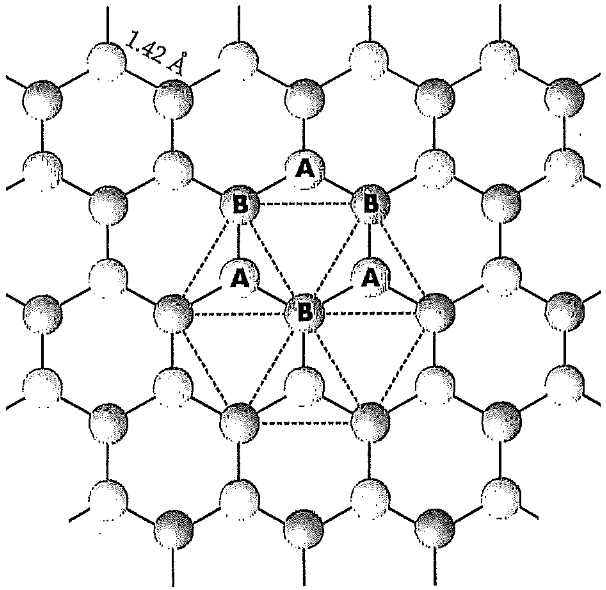
delocalized π-electrons

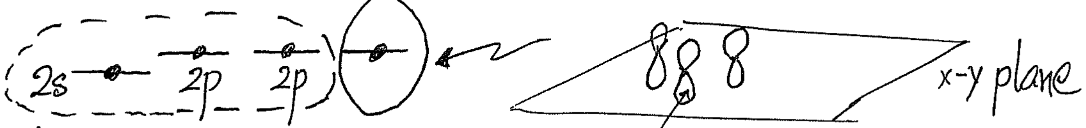
c



Graphene: A single atomic layer of carbon

[A. Geim and K. S. Novoselov: 2010 Nobel Physics Prize]





these 3 electrons formed covalent bonds with neighboring atoms

⇓

locked into bonds

⇓

they can't move around after forming bonds

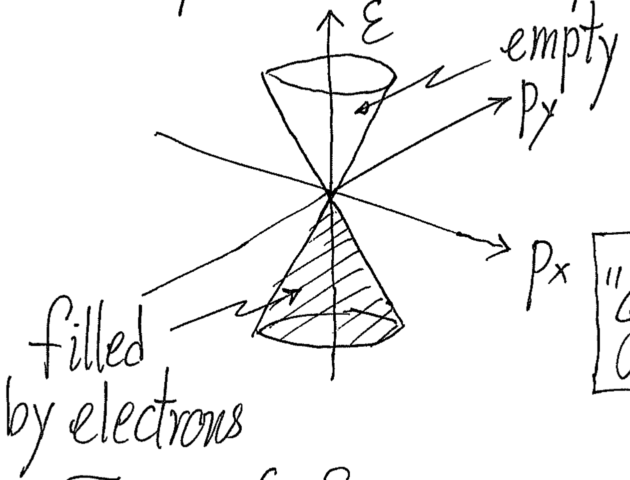
each carbon has one electron in a $2p_z$ state 8 perpendicular to the graphene sheet (π electrons)

π electrons can move on sheet!

- All are carbon atoms
- Labels A and B for atoms that see different environments

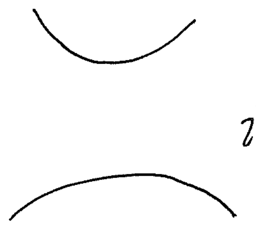
The π electrons in Graphene *behave unusually*!

- They move around "above and below" the sheet
- In a solid, electron states form bands described by $\overset{\text{energy}}{\varepsilon}(\underset{\text{momentum of electron}}{p})$
- Graphene has $\varepsilon(p)$ of the form[†]



"gapless semiconductor"

c.f.



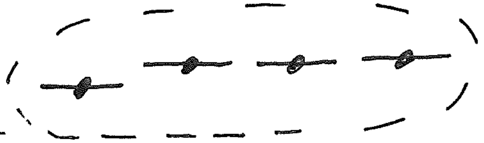
Form of $\underbrace{\varepsilon = vp}$ [c.f. $\varepsilon^2 = m^2c^4 + c^2p^2 \Rightarrow \varepsilon = cp$ for massive particle]

[like massless fermions!] (Table-top QED system?)

[†] This is LCAO applied to solids, often called tight-binding model in energy band theory (solid state physics)

(i) sp^3 Hybridization [Pauling 1928, Nobel Chemistry Prize 1954]

- CH_4, diamond, silicon, ... (semiconductor industry)
- Carbon (again)



$$2s^2 2p^2 \rightarrow \underbrace{2s^1 2p_x^1 2p_y^1 2p_z^1}_{\text{all in}}$$

→ 4 electrons available for forming bonds

→ one s AO and three p AO's combine to form Four Hybrid Orbitals (sp^3 hybrid orbitals)

Formally, construct Hybrid Orbitals

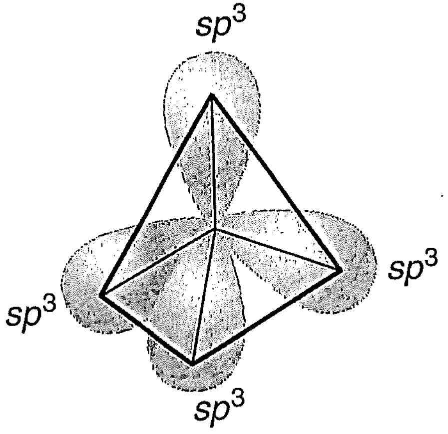
$$\psi_i = \frac{1}{\sqrt{4}}\psi_s + b_i \psi_{p_x} + c_i \psi_{p_y} + d_i \psi_{p_z} \qquad (30)$$

($i = 1, 2, 3, 4$) require ψ_i to be normalized and mutually orthogonal

The end results are

$$\boxed{\begin{aligned}\psi_1 &= \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})\\ \psi_2 &= \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})\\ \psi_3 &= \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})\\ \psi_4 &= \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})\end{aligned}} \quad (31)$$

sp^3 hybrid orbitals



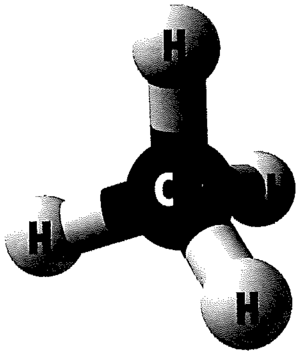
Angle between orbitals $= 109.5°$ (Ex.)

These are the <u>four</u> sp^3 <u>Hybrid Orbitals</u>

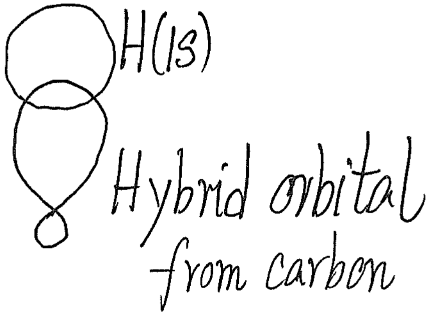
- Highly directional
- Like four vectors in $\left\{\begin{array}{ll}(+1,+1,+1) & [\hat{x}+\hat{y}+\hat{z}]\\ (-1,-1,+1) & [-\hat{x}-\hat{y}+\hat{z}]\\ (+1,-1,-1) & [\hat{x}-\hat{y}-\hat{z}]\\ (-1,+1,-1) & [-\hat{x}+\hat{y}-\hat{z}]\end{array}\right\}$ directions (or rotated as a whole)

What for? To lower energy by forming bonds

Methane CH_4



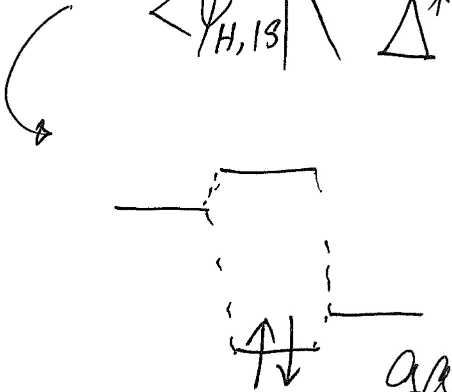
For each hybrid orbital (say ψ_1), there is one electron ready for bonding.



$$\begin{array}{c|cc} & |\psi_i\rangle & |\psi_{H,1s}\rangle \\ \hline \langle\psi_i| & \varepsilon_i & \Delta \\ \langle\psi_{H,1s}| & \Delta^* & \varepsilon_{H,1s} \end{array}$$

Δ is made bigger by

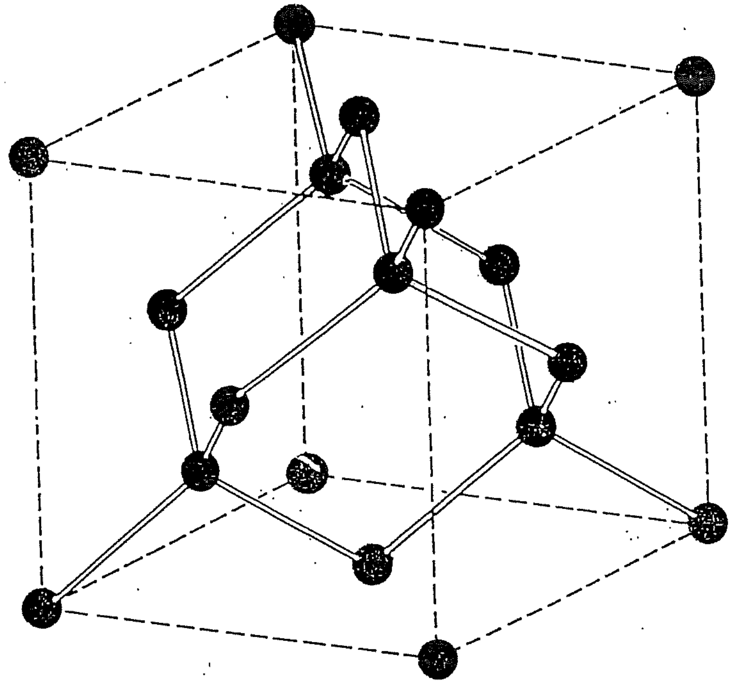
- Hybrid orbital focuses electron towards $\psi_{H,1s}$
- Hybrid orbitals spread electrons farther apart



gain energy for each σ-bond formed

[Same physics works!]

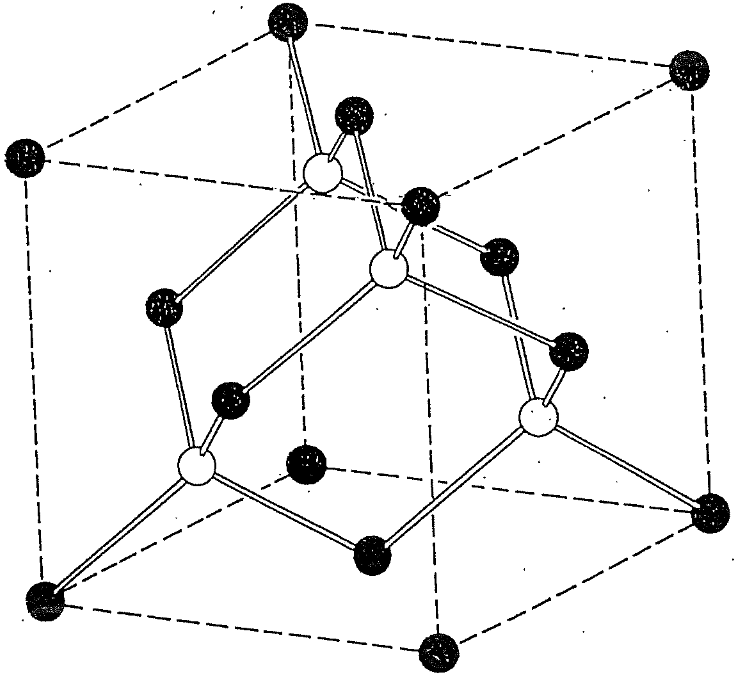
sp^3 Hybridization governs many semiconductors' structure



Diamond Structure

- Same atom at every ●

  [e.g. carbon, <u>silicon</u>, germanium] ←

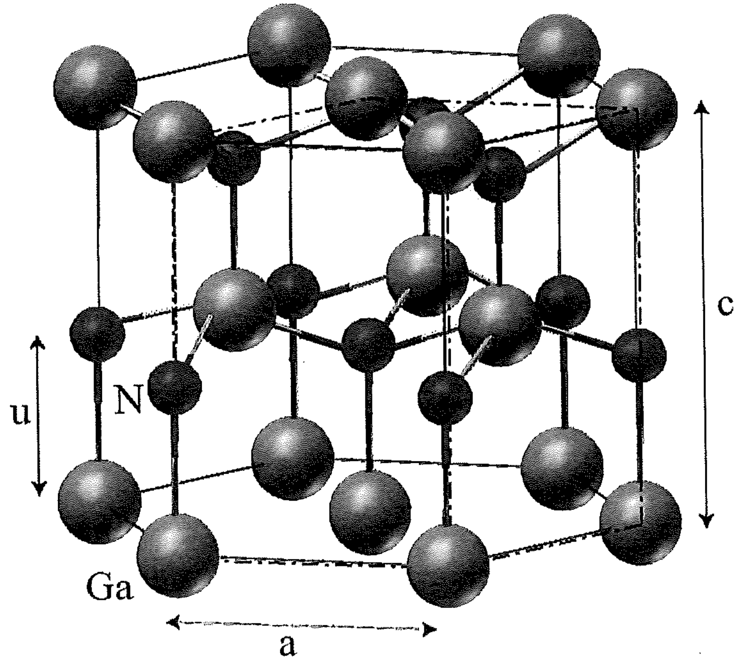


Zinc Blende Structure

● A atom ○ B atom

[e.g. GaAs (III-V semiconductor)
CdTe (II-VI Semiconductor)]

Most important materials! →



Wurtzite Structure

E.g. $\underbrace{\text{GaN}}$, ZnO

blue LED & blue laser

[2014 Nobel Physics Prize]

used in your mobile phone

sp^3 Hybridization gives crystal structures of important semiconductors

AND the structures determine the bands and band gaps

A bit of Quantum Mechanics takes us into the fascinating world of molecules, solids, and materials science.

Take-Home Messages

- QM, LCAO-MO, "Variational Method ↔ Matrix Math" (often 2x2) explain much of the world of materials (molecules & solids)
- Put binding (ionic, covalent bonds), hybridization, σ and π bonds, Huckel theory (π-electrons) under one roof (just QM)
- A little idea (solid foundation needed though) that does a lot of things!

Robert S. Mulliken and Friedrich Hund[+] developed Molecular Orbital Theory

- 1927 at Göttingen (worked in Born's group)
- Mulliken developed LCAO

1966 Nobel Chemistry Prize to Mulliken
"for his fundamental work concerning bonds and the electronic structure of molecules by the molecular orbital theory"

[Hund was left out, but Mulliken said he would have glady shared the Prize with Hund.]

Mulliken (left) and Hund

[+] Hund's contributions also included the Hund's rules.

An interesting comment by Dirac in 1929 on physics and chemistry

P. A. M. Dirac, Proceedings of the Royal Society A 123, 714 (1929)
(p. 714-733)

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Already before the arrival of quantum mechanics there existed a theory of atomic structure, based on Bohr's ideas of quantised orbits, which was fairly successful in a wide field. To get agreement with experiment it was found

Should appreciate that up to now, work and progress continue to be made in how to perform QM calculations more accurately and efficiently for the understanding of molecules (many biology related)