# Extensions on Bonding

- LCAO is a very useful/general approach [back up by QM, variational method]
- Can cleverly extend to understand bonding that involves

sp , $sp^2$ , $sp^3$ hybridization
[e.g. $BeH_2$] [$C_2H_4$, graphene] [$CH_4$, diamond, semiconductors]

and

[benzene]

"what is that "○" in the middle?"

# H. Hybridization and Hybrid orbitals

- Why are there $BeH_2$, $CH_4$, ..., $C_{60}$, graphene (1 layer of carbon)?
- Structure of diamond (carbon), silicon, ... [semiconductors]?
- Key ideas: sp, $sp^2$, $sp^3$ hybrid orbitals [What are they?]
- Just LCAO
- Hybrid orbitals: Special linear combinations of atomic orbitals with atomic orbitals from the SAME atom

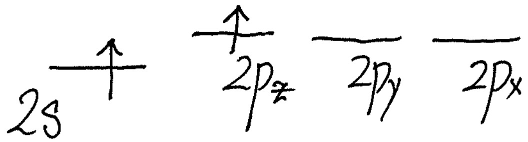
What for? FOR Bonding with another atom

# Concept of hybridization introduced via sp hybridization: $BeH_2$

- $BeH_2$ exists (fact)
- But Be has $1s^2 \underbrace{2s^2}_{\text{full (closed shell)}}$, how come?

- Description in Pictures

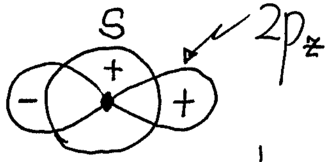
Be



[needs some energy, could gain back via bonding later]

(could be $p_x$, $p_y$)

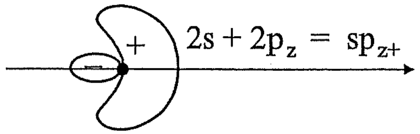
Be



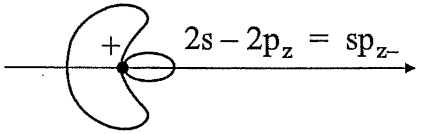
same atom

2 electronic states

2 electronic states (including spin)

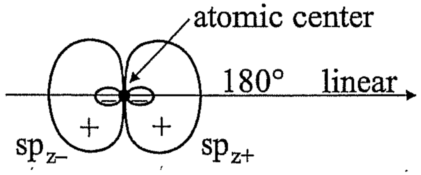


$\psi_{2s} + \psi_{2p_z}$



$\psi_{2s} - \psi_{2p_z}$

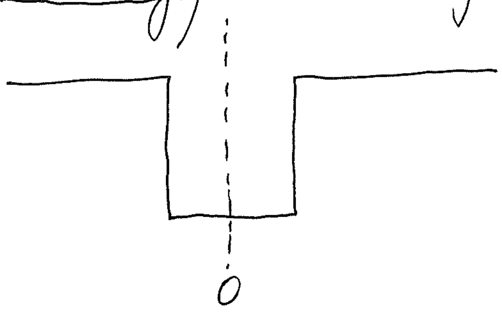
$\boxed{\text{sp hybridization}}$



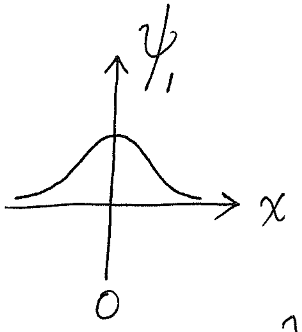
Also 4 electronic states [no more, no less]

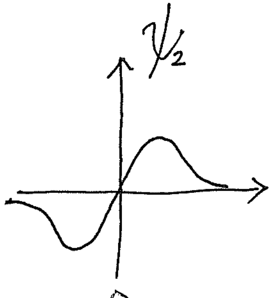
two hybrid orbitals of Be point in opposite directions

## Analogy : 1D finite well



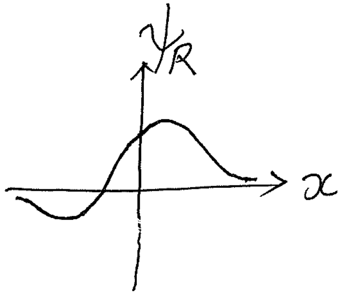
Ground state (like s)

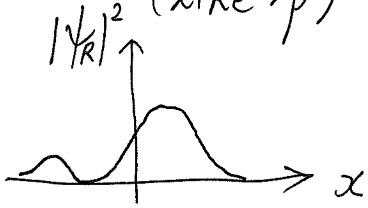




1st excited state (like p)

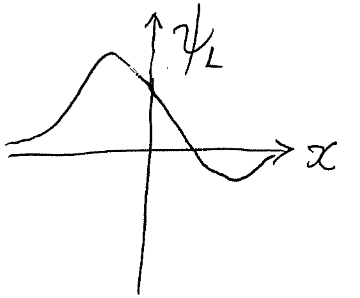
$\psi_R \propto \psi_1 + \psi_2$ [like $\psi_s + \psi_p$]

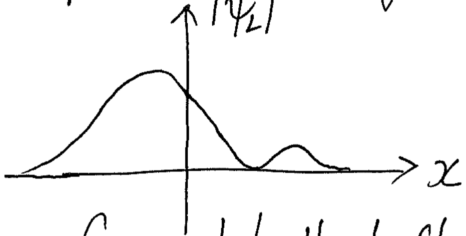




focused to the <u>Right</u>

$\psi_L \propto \psi_1 - \psi_2$ [like $\psi_s - \psi_p$]





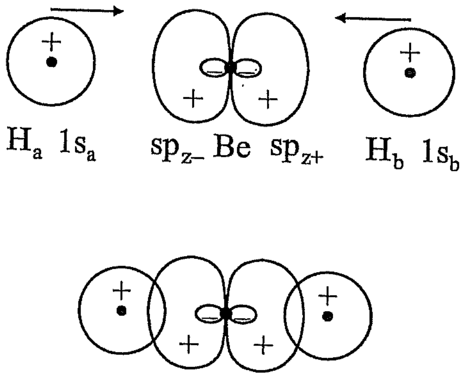
focused to the <u>Left</u>

To prepare for forming bonds with atoms in the right (using $\psi_R$) and in the left (using $\psi_L$)

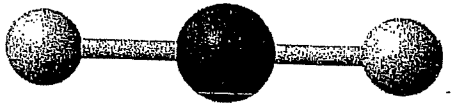
- The atomic s orbital will <u>not</u> bias any one of the "sp" hybrid orbitals, i.e. there is a fair share of $\psi_s$ between the two hybrid orbitals.
- Besides pointing at different directions, the hybrid orbitals are equivalent.

<u>What for?</u> Prepare for Bonding [to lower energy]

$BeH_2$:

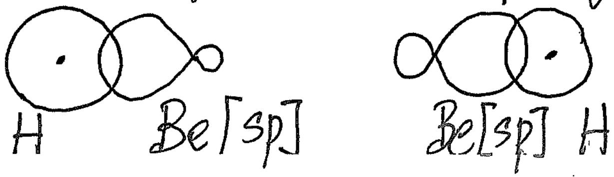


$BeH_2$



[energy is lowered]

- Spread out electrons [suppress el-el repulsion]
- highly <u>directional</u>
- Strong bonds
  - Good overlap of



- "Hybridization" is just a way to <u>describe the wavefunction</u> of <u>Be</u>, it is <u>not</u> an event

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

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

Be <u>atomic orbitals</u>

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

<u>Description 1</u> : Easy! 2 electrons in two states

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_s(1) & \psi_p(1) \\ \psi_s(2) & \psi_p(2) \end{vmatrix} \qquad (24)$$

satisfies anti-symmetric requirement

[in terms of atomic orbitals $\psi_s$ and $\psi_p$ (<u>same atom</u>)]

## Description 2 : Introduce "Hybrid orbitals"

$$\psi_A = \frac{1}{\sqrt{2}}(\psi_s - \psi_p) \quad ; \quad \psi_B = \frac{1}{\sqrt{2}}(\psi_s + \psi_p) \qquad (25)$$

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

▪ $\psi_A$ , $\psi_B$ are the sp hybrid orbitals

With 2 electrons, we could as well say that "one electron in $\psi_A$ and one electron in $\psi_B$"

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_A(1) & \psi_B(1) \\ \psi_A(2) & \psi_B(2) \end{vmatrix} \qquad (26)$$

[in terms of hybrid orbitals]

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

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

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

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

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

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

They Describe the same wavefunction!

(∴ Hybridization is nothing fancy!)

# Properties

Meaning: $\underbrace{\int \psi_s^* \psi_p}\, d\tau = 0$

- $\psi_s$ , $\psi_p$ are AO's of Same atom ⇒ they are orthogonal
- $\psi_A , \psi_B$ are orthogonal (Ex.) [Mathematical Meaning: $\int \psi_A^* \psi_B \, d\tau = 0$]

[About two wavefunctions' integral]

- Geometrically (in real space), $\psi_A$ and $\psi_B$ point to opposite directions

$$\psi_A = \frac{1}{\sqrt{2}} \big( \underbrace{\psi_s}_{\text{no direction}} \underbrace{- \psi_p}_{\text{point at } -\hat{z} \text{ direction}} \big)$$

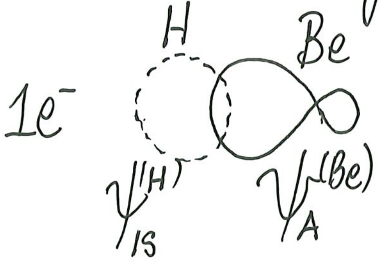
$$\psi_B = \frac{1}{\sqrt{2}} \big( \psi_s + \underbrace{\psi_p}_{\text{point at } +\hat{z} \text{ direction}} \big)$$

$\boxed{\text{Equal share (same } \tfrac{1}{\sqrt{2}} \text{ factor) of } \psi_s \text{ in } \psi_A \text{ and } \psi_B}$

$\leftarrow \psi_A$ $\qquad$ $\rightarrow \psi_B$

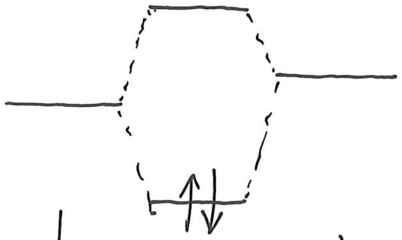
dot product of vectors $= -1$ ⇒ 180° apart

# Gain Energy by forming bonds (BeH$_2$) [see optional appendix for details]



$$\begin{array}{cc} & \begin{array}{cc}\psi_A^{(Be)} & \psi_{1s}^{H}\end{array} \\ \begin{array}{c}\psi_A^{*(Be)} \\ \psi_{1s}^{(H)}\end{array} & \begin{pmatrix}\varepsilon^{(Be)} & \Delta \\ \Delta & \varepsilon^{(H)}\end{pmatrix}\end{array}$$

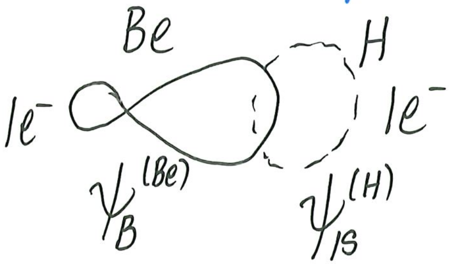
($\Delta$ becomes bigger)



stronger pushing lowers energy

H — Be ---- H

↑ this bond



$$\begin{pmatrix}\varepsilon^{(Be)} & \Delta \\ \Delta & \varepsilon^{(H)}\end{pmatrix}$$

($\Delta$ becomes bigger)

stronger pushing lowers energy

H ---- Be — H

↑ this bond

# $sp^2$ Hybridization

$C_2H_4$ (ethylene)

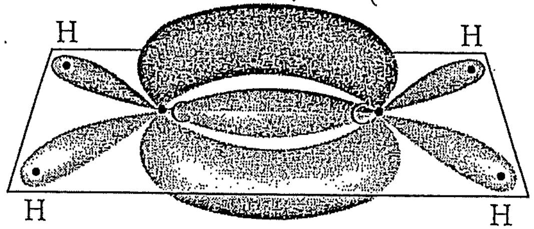
$C: 2s^2 2p^2$

for forming hybrid orbitals

2s —•— —•— —•— —•— 2p

$sp^2$ hybridization

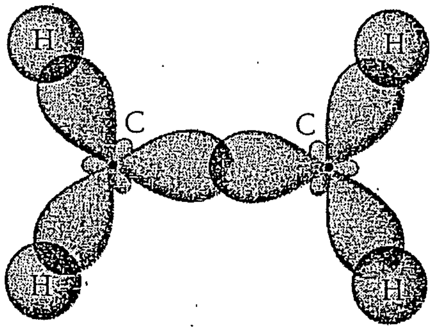
double (one σ and one π) bond



(a)

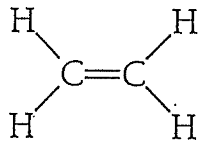
(a) The ethylene ($C_2H_4$) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the $sp^2$ hybrid orbitals that form σ bonds between the C atoms and between each C atom and two H atoms. (c) Side view, showing the pure $p_x$ orbitals that form a π bond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

Top View



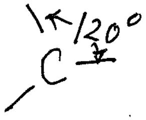
(b)

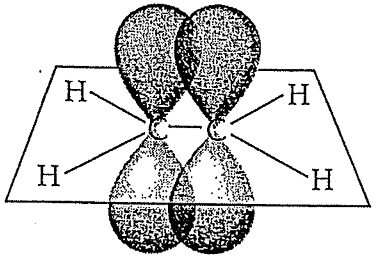
Ethylene



Again, highly directional

[120° between bonds.]



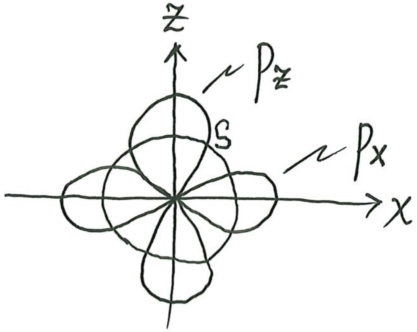


(c)

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

- Get a sense! How <u>one</u> 2s and <u>two</u> 2p AO's could linearly combine to form <u>three equivalent</u> $sp^2$ hybrid orbitals?

$\psi_{2s}, \psi_{2p_x}, \psi_{2p_z}$ (say) [carbon] (1 electron remains in $\psi_{2p_y}$)



<u>Formally</u>: form three linear combinations

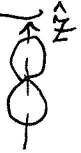
$$
\begin{aligned}
\xi_1 &= a_1\psi_{2s} + b_1\psi_{2p_z} + c_1\psi_{2p_x} \\
\xi_2 &= a_2\psi_{2s} + b_2\psi_{2p_z} + c_2\psi_{2p_x} \qquad (27) \\
\xi_3 &= a_3\psi_{2s} + b_3\psi_{2p_z} + c_3\psi_{2p_x}
\end{aligned}
$$

[$\xi_1, \xi_2, \xi_3$ are to become hybrid orbitals]

Key ideas

- The s AO will be shared <u>equally</u> among $\xi_1, \xi_2, \xi_3 \Rightarrow \boxed{a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}}$
- $\xi_1, \xi_2, \xi_3$ should be <u>normalized</u> and <u>orthogonal</u> to each other

Recall: $\psi_{2s} \sim R(r)$ ; $\psi_{2p_z} \sim \sqrt{3}\,R(r)\underbrace{\cos\vartheta}$ ; $\psi_{2p_x} \sim \sqrt{3}\,R(r)\sin\vartheta\cos\phi$



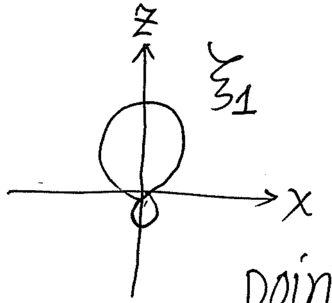
- Place $\xi_1$ along $\hat{z}$-direction (still general)

$$\xi_1 = \frac{1}{\sqrt{3}}\psi_{2s} + b_1\psi_{2p_z}$$

(Note: $\psi_{2s}$ & $\psi_{2p_z}$ are orthogonal)

Require $\xi_1$ to be normalized $\Rightarrow b_1 = \sqrt{\frac{2}{3}}$

$$\therefore \boxed{\xi_1 = \frac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\psi_{2p_z}} \quad (28a)$$



pointing in z-direction

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

$\xi_2$ orthogonal to $\xi_1 \Rightarrow \frac{1}{3} + \sqrt{\frac{2}{3}}\,b_2 = 0 \Rightarrow b_2 = -\frac{1}{\sqrt{6}}$

$\xi_2$ is itself normalized $\Rightarrow c_2 = \frac{1}{\sqrt{2}}$ (Ex.)

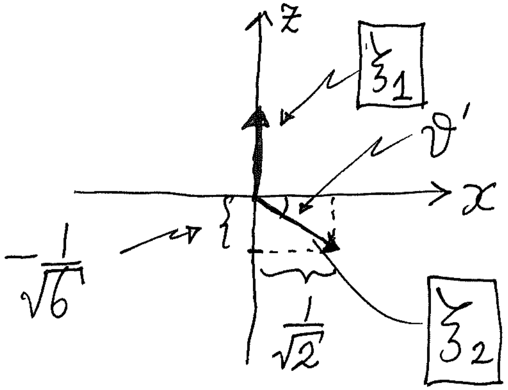
$$\boxed{\xi_2 = \frac{1}{\sqrt{3}}\psi_{2s} - \frac{1}{\sqrt{6}}\psi_{2p_z} + \frac{1}{\sqrt{2}}\psi_{2p_x}} \quad (28b)$$

- Ex: Construct $\xi_3$

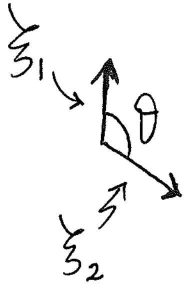
<u>Question:</u> <u>Which direction does $\xi_2$ point at?</u>

<u>Lazy way</u> (that works) $\xi_1 = \underbrace{\frac{1}{\sqrt{3}}\psi_{2s}}_{\text{no direction}} + \sqrt{\frac{2}{3}}\underbrace{\psi_{2p_z}}$ like a vector in $\hat{z}$ direction

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



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



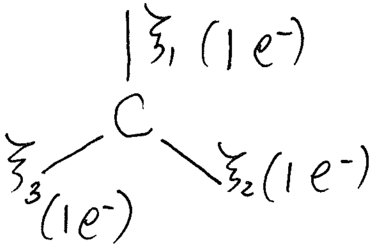
$$\boxed{\theta = 90° + 30° = 120°}$$

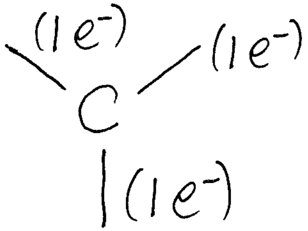
[Again, <u>QM</u> is behind directionality]

- Ex: Where does $\xi_3$ point at?

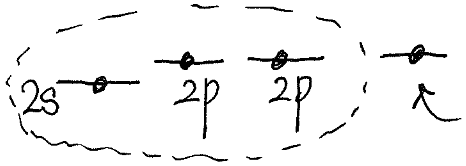
## Consequences

- Plane of hybrid orbitals



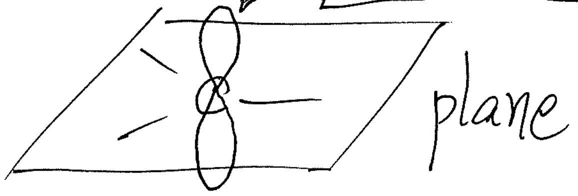


$sp^2$ hybridization provides the skelation (framework) of forming strong σ-bonds (direction) and dictates the structure

- 

2p state perpendicular to covalent bond structure

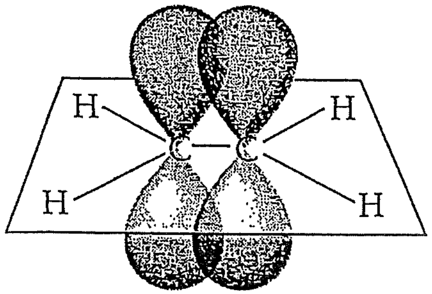
one electron in 2p



Important!

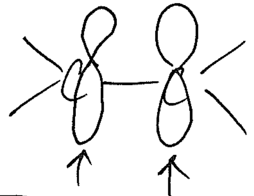
- can form π-bond
- can delocalize (moving around) (e.g. graphene)

$C_2H_4$



# Quick QM thinking on π-bond

- After forming the strong σ-bonds skeleton

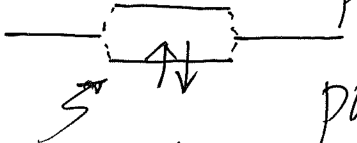


| | |
|---|---|
| 1e | 1e |
| (2p) | (2p) |
| (left) | (right) |

These electrons are called π electrons

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

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



push up

push down

π-bond

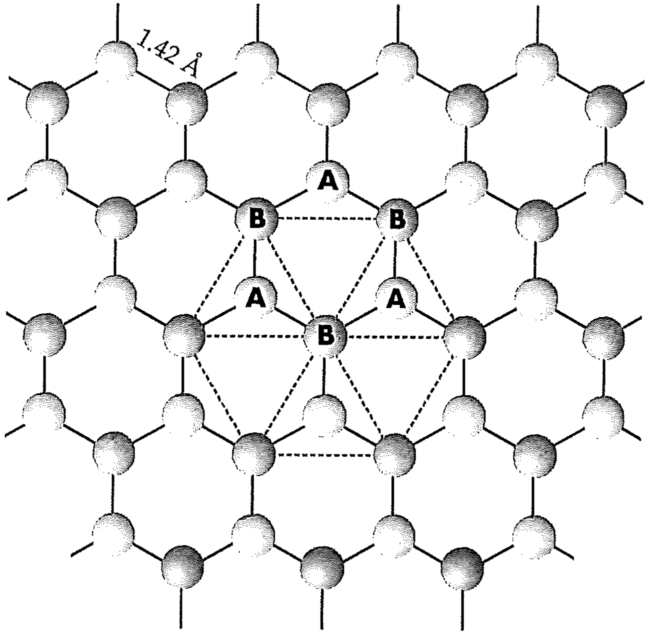
(Done!)

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

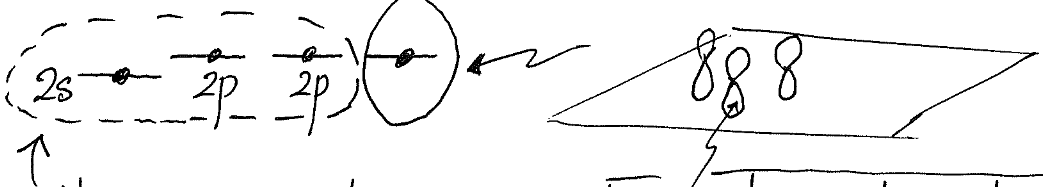
⇒ pushing is smaller ⇒ weaker than σ-bond.

# Graphene: A single atomic layer of carbon

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



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



these 3 electrons formed covalent bonds with neighboring atoms

⇓

locked into bonds

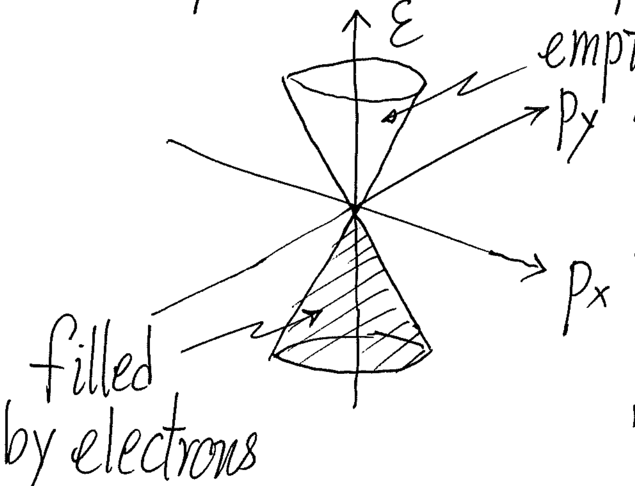
⇓

they can't move around after forming bonds

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

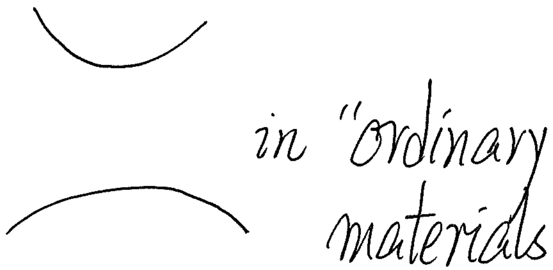
# The $\pi$ electrons in Graphene <u>behave unusually</u>!

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



"gapless semiconductor"

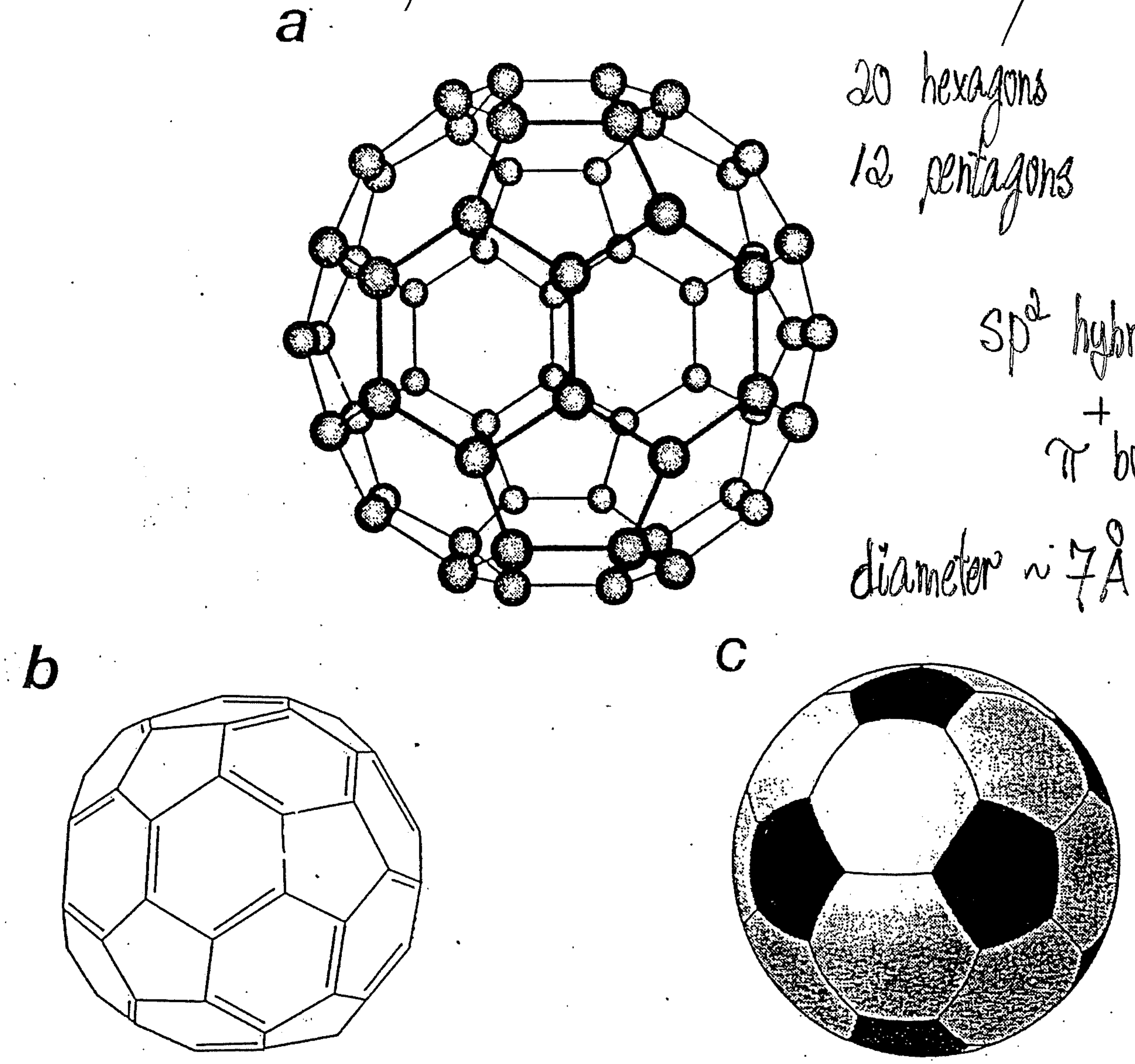
c.f.



Form of $\underbrace{\varepsilon = v\underline{p}}$ [c.f. $\varepsilon^2 = m^2c^4 + c^2p^2 \Rightarrow \varepsilon = cp$ for <u>massive</u> particle]

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

# C$_{60}$ molecule ["Bucky Ball"] [Kroto and Smalley: 1996 Nobel Chemistry Prize]



20 hexagons

12 pentagons

sp$^2$ hybridization
+
π bonds

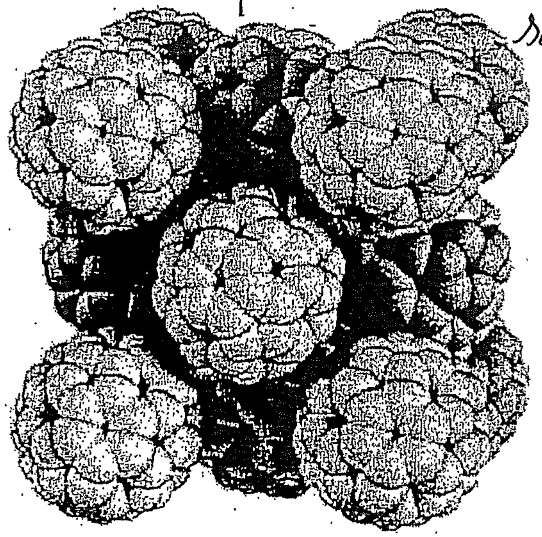
diameter ~ 7Å

The structure of the sixty-carbon-atom cluster, called buckminsterfullerene (a), and the pattern of single and double bonds which allows all of the atoms to form four bonds (b). Each carbon atom in the cage is equivalent. The pattern of hexagons and pentagons in this highly symmetrical shape is the same as that in a soccer ball (c).

# Properties of solid $C_{60}$

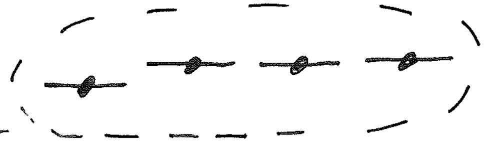
| | |
|---|---|
| Density | 1.7 g/cm$^3$ |
| Crystal structure | Facc-centered cubic |
| Nearest-neighbor distance | 10.04 Å |
| Cage diameter | 7.1 Å |
| Lattice constant | 14.198 Å |
| Index of refraction | 2.2 at 630 nm wavelength |
| Infrared-active modes | 1429, 1183, 577, 528 cm$^{-1}$ |
| Bulk modulus | 18 gigapascals |
| Ionization potential | 7.6 eV |
| Cohesive energy | |
| per $C_{60}$ molecule | 1.5 eV |
| per atom | 7.4 eV |
| Electrical conductivity | Nonconductor |
| Electron bandgap | 1.5 eV |
| Effective mass of conduction band electron | 1.3 $m_e$ |
| Superconducting $T_c$ | |
| $K_3C_{60}$ | 19 K |
| $Rb_3C_{60}$ | 29 K |
| $Cs_2RbC_{60}$ | 33 K |
| $Rb_{2.7}Tl_{2.2}C_{60}$ | 42.5 K |

$C_{60}$ molecules forming a face-centered cubic solid



## $sp^3$ Hybridization [Pauling 1928, Nobel Chemistry Prize 1954]

- $CH_4$, diamond, silicon, ...
- Carbon (again)



$2s^2 2p^2 \rightarrow 2s^1 2p_x^1 2p_y^1 2p_z^1$

→ 4 electrons available for forming bonds

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

Formally, construct Hybrid Orbitals

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

($i = 1, 2, 3, 4$) require $\psi_i$ to be <u>normalized</u> and <u>mutually orthogonal</u>

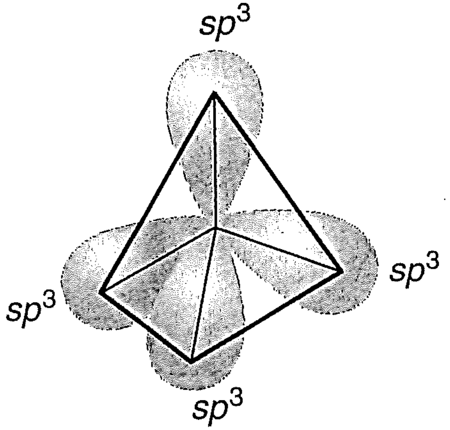
The end results are

$$\psi_1 = \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})$$

$$\psi_2 = \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})$$

$$\psi_3 = \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})$$

$$\psi_4 = \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})$$



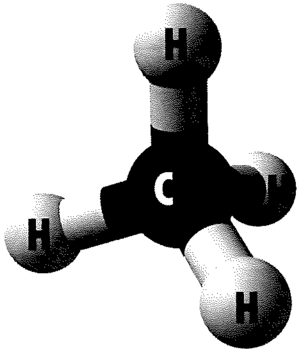
These are the <u>four</u> sp³ <u>Hybrid Orbitals</u>

Angle between orbitals = 109.5° (Ex.)

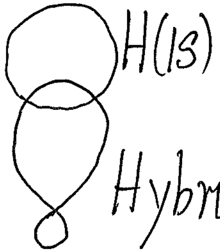
- Highly directional
- Like four vectors in $\left\{\begin{matrix} (+1,+1,+1) & [\hat{x}+\hat{y}+\hat{z}] \\ (-1,-1,+1) & [-\hat{x}-\hat{y}+\hat{z}] \\ (+1,-1,-1) & [\hat{x}-\hat{y}-\hat{z}] \\ (-1,+1,-1) & [-\hat{x}+\hat{y}-\hat{z}] \end{matrix}\right\}$ directions (OR rotated as a whole)

## What for? To lower energy by forming bonds

Methane $CH_4$



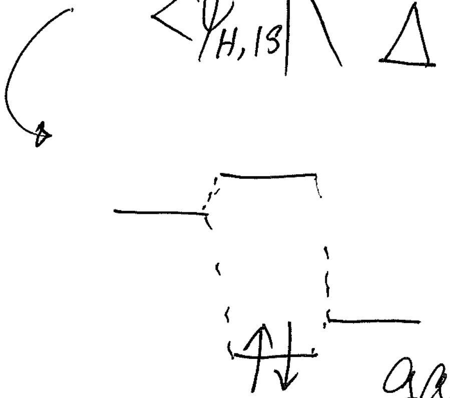
For each hybrid orbital (say $\psi_1$), there is one electron ready for bonding.



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

Δ is made bigger by

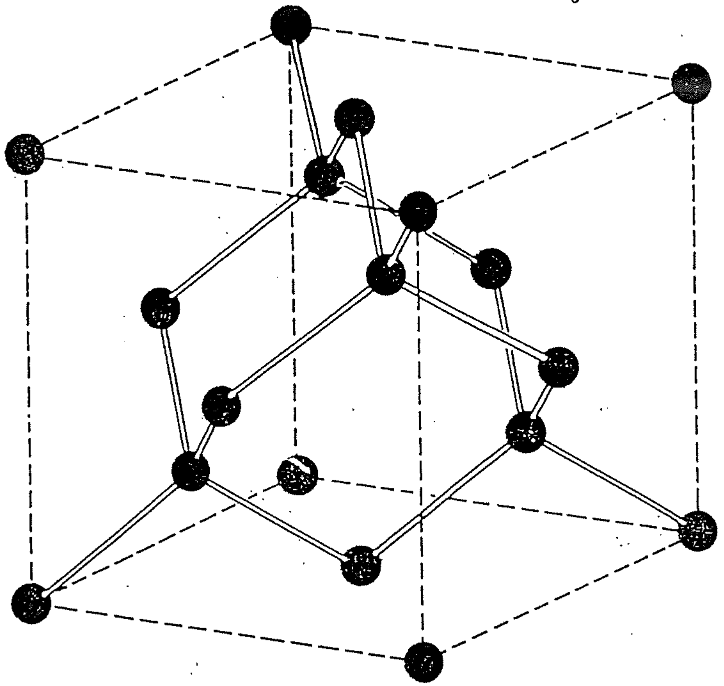
- Hybrid orbital focuses electron towards $\psi_{H,1s}$
- Hybrid orbitals spread electrons farther apart



gain energy for each σ-bond formed

[Same physics works!]

# $sp^3$ Hybridization governs many semiconductors' structure

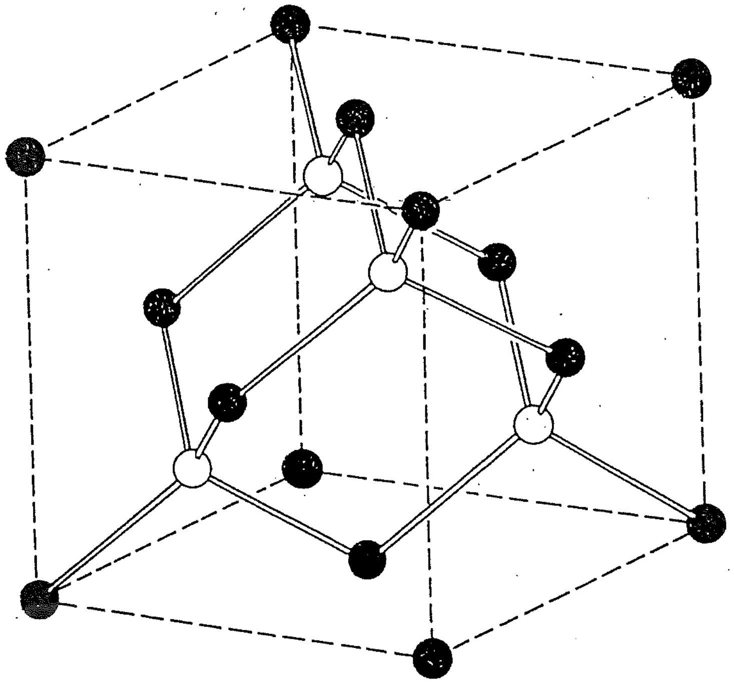


Diamond Structure

- Same atom at every ●

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

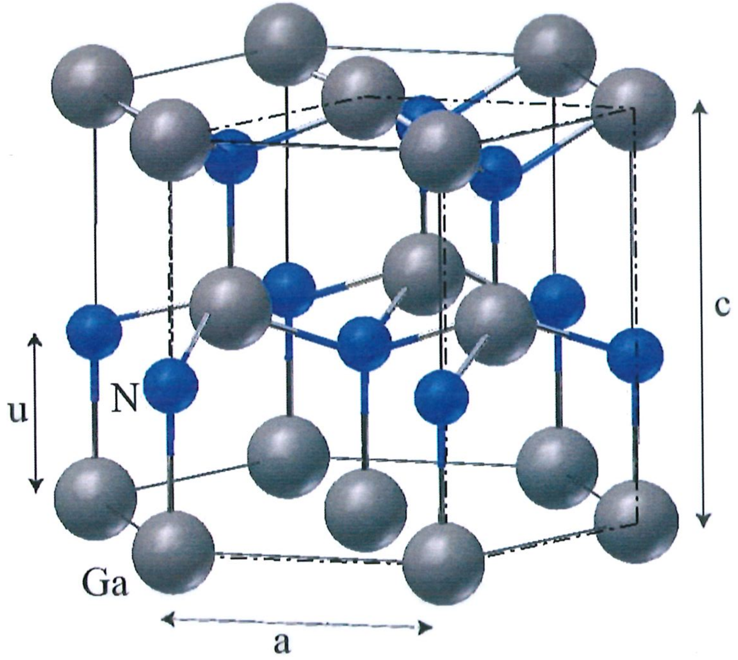
Most important materials! →



Zinc Blende Structure

● A atom ○ B atom

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



Wurtzite Structure

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

blue LED & blue laser

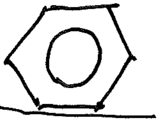
[2014 Nobel Physics Prize]

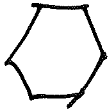
used in your mobile phone

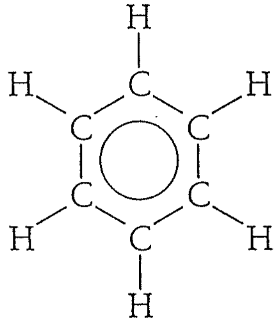
$sp^3$ Hybridization gives crystal structures of important semiconductors

AND the structures determine the bands and band gaps

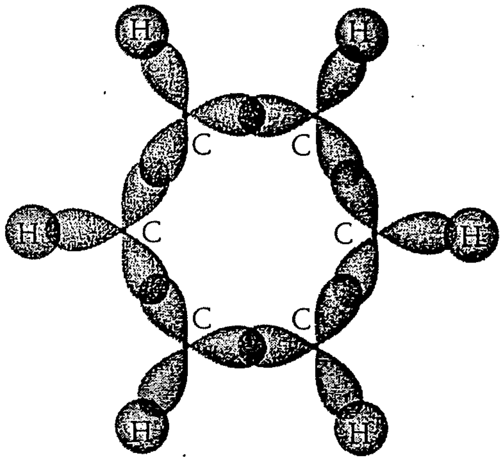
A bit of Quantum Mechanics takes us into the fascinating world of molecules, solids, and materials science.

# I. What is the "O" in benzene  ?

- $C_6H_6$ : The skeleton  is governed by $sp^2$ hybridization

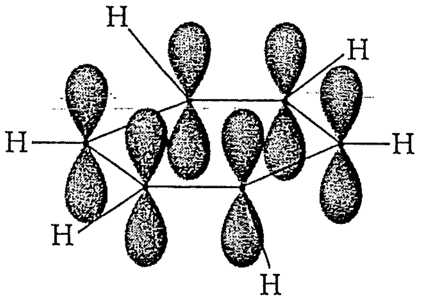


these strong bonds locked in the electrons

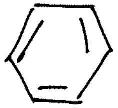
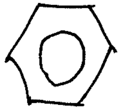


- $sp^2$
- σ bonds form framework 

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

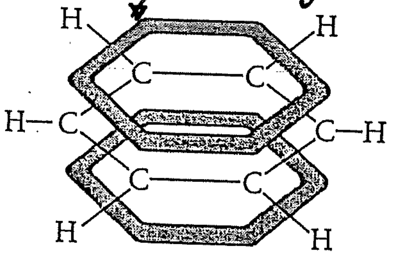


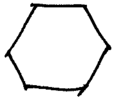
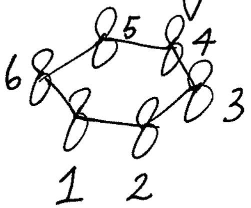
Behavior of six π-electrons?

 OR  VS 

[Quantum Mechanics Approach?]

delocalized π electrons



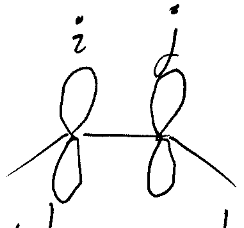
- Framework  is rigid and strong
- Q: Behavior of $p_z$ electrons 

(one electron each, six $p_z$ electrons)

- How do they form bonds? LCAO

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, $\left| H_{ij} - E S_{ij} \right| = 0$ $(i, j = 1, 2, \cdots, 6)$ gives 6 values of $E$ for 6 $p_z$ electrons to fill in
- Practically, $S_{ii} = 1$

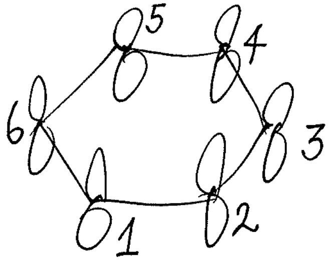
  $S_{ij} \approx 0$ 

"Not much overlap"

and $H_{ij}$ more important

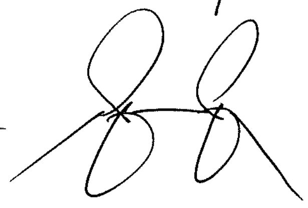
- $H_{ii}$ is mainly governed by the atomic $\varepsilon_{2p}$ energy

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

- 

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

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

- For two nearest neighboring  $H_{ij} = \underbrace{V}_{\text{same between two nearest neighbors}}$

$\therefore$ Need only two terms:

$\varepsilon$ and $V$

$\underbrace{(\text{OR } \alpha) \qquad (\text{OR } \beta)}_{\text{in Chemistry books}}$ [$\beta < 0$ typically]

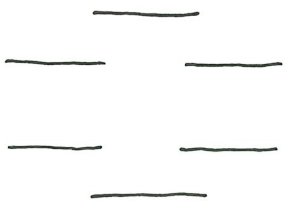
$$\begin{vmatrix} \varepsilon - E & V & 0 & 0 & 0 & V \\ V & \varepsilon - E & V & 0 & 0 & 0 \\ 0 & V & \varepsilon - E & V & 0 & 0 \\ 0 & 0 & V & \varepsilon - E & V & 0 \\ 0 & 0 & 0 & V & \varepsilon - E & V \\ V & 0 & 0 & 0 & V & \varepsilon - E \end{vmatrix} = 0$$

gives six values of $E$

or written as a 6×6 matrix problem

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

- Six values of E are lined up as

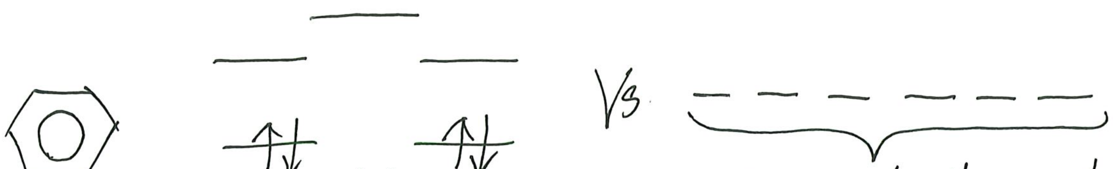


(Ex.)

(there are MO's for π electrons)

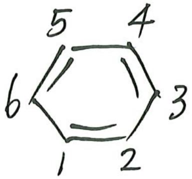
- There are 6 π electrons

(Pauli Principle)



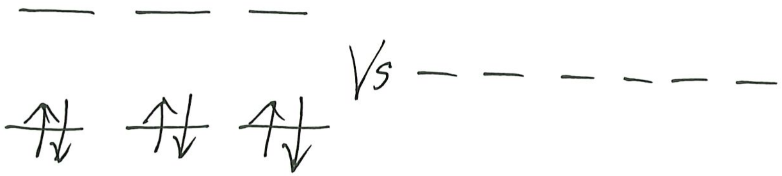
(lower energy)

if $p_z$'s don't couple

- How about  ?

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

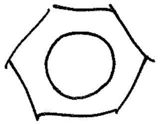
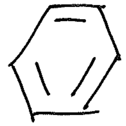
$\Rightarrow$ Eigenvalues



(higher energy than )

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

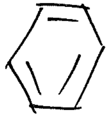
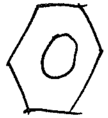
[becomes three identical 2x2 problems]

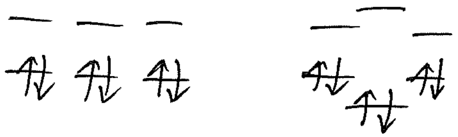
-  has a lower energy than  and 

"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 $H_{ii}$ and nearest-neighboring $H_{ij}$

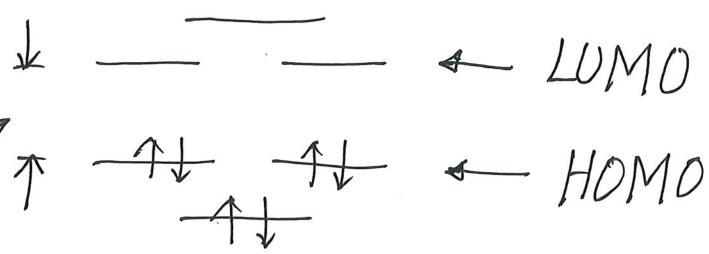
$(\varepsilon)$ $(V)$

$(\alpha)$ $(\beta)$

- **LUMO - HOMO Difference**

LUMO: lowest unoccupied molecular orbital

HOMO: highest occupied molecular orbital



LUMO-HOMO energy difference[†]

controls material's absorption/emission frequency

- How about butadiene?

 OR  OR something else?

- Behavior of $p_z$ (OR $\pi$) electrons in graphene, $C_{60}$?
- Delocalizing is key to physics of metals

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