C. LCAO (Linear Combination of Atomic Orbitals)

Bonding in Molecules / extended to solids

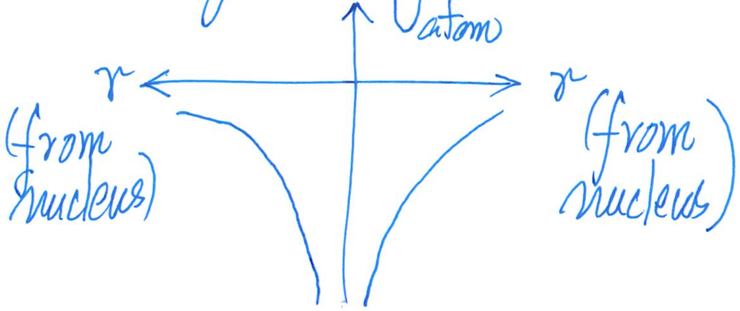
Same idea: Reduce to single-electron problem

- $\underbrace{\text{solve Schrödinger Equation}}_{\text{molecular orbitals (MO's)}}$, fill electrons

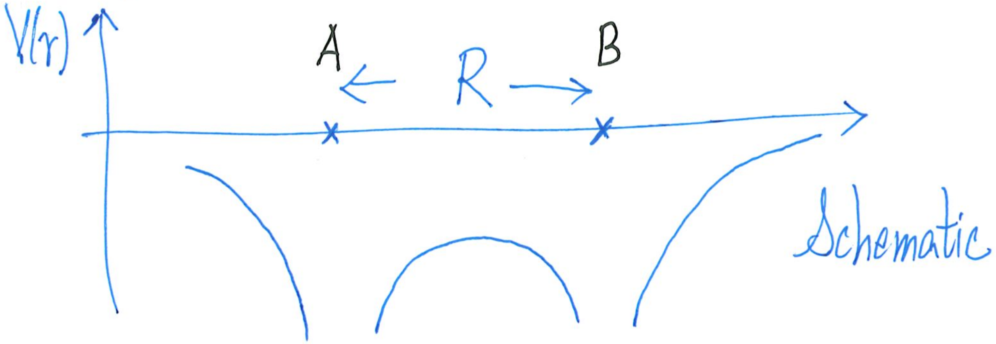
$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r})}_{\text{not periodic in a molecule}} \qquad (1b)$$

Example

- Single atom



(a) Diatomic Molecule



Idea

- Use atomic orbital(s) from atoms forming the molecule as basis functions for expanding the solution to TISE

- Physical consideration
    - Which atomic orbital (and its electron(s)) will be involved in bonding? (Valence electrons, those will involve in bonding)

E.g. H_2 molecule (homonuclear diatomic molecule)

$$\psi(\vec{r}) = C_L \underset{\uparrow}{\phi_{1s}^{(L)}} + C_R \underset{\nearrow}{\phi_{1s}^{(R)}} \quad (17) \leftarrow$$

This is an approximation! (In general, include all AO's from both atoms)

1s AO's, but centered at Different nuclei

(In general, $\int \phi_{1s}^{*(L)}(\vec{r})\, \phi_{2s}^{(R)}(\vec{r}-\vec{R})\, d^3r \neq 0$, although it is often ignored)

With $\hat{H}$ and $\psi = c_L \phi_{1s}^{(L)} + c_R \phi_{1s}^{(R)}$, then

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

In principle, H_{ij} and S_{ij} can be evaluated!

In reality, evaluating H_{ij} and S_{ij} from first principles is hard
(can be done in H_2^+ and H_2 where H-atom 1s wavefunction is known)
(recall: finding AO's of atoms beyond hydrogen is non-trivial)

But not giving up! LCAO provides physically transparent picture of bonding!

<u>Aim</u>: Convey Physical Sense on LCAO approach

Think in simplest way! $S_{11} = 1$, $S_{22} = 1$ (true, same center, normalization)

Approximately, $S_{12} \cong 0$, $S_{21} \cong 0$ (again, generally not[+] true)

Look at $H_{11} = \int \phi_{1s}^{(L)*}(\vec{r})\, \hat{H}\, \phi_{1s}^{(L)}(\vec{r})\, d^3r$

$$\sim \int \phi_{1s}^{(L)*}(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + U_{\text{atomic}}(\vec{r}) \right] \phi_{1s}^{(L)}(\vec{r})\, d^3r - \int \phi_{1s}^{(L)*}(\vec{r}) \left[U_{\text{atomic}}(\vec{r}) - V(\vec{r}) \right] \phi_{1s}^{(L)}(\vec{r})\, d^3r$$

not precise to all factors

centered at "LHS" as argument is $(\vec{r} - \vec{0})$

$$\sim \mathcal{E}_{1s}^{\text{atom}} \underbrace{- (\text{a number})}_{\text{a shift (c.f. 1st order perturbation)}}$$

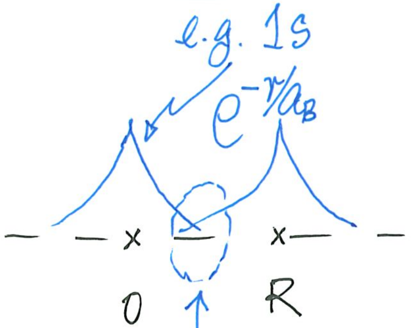
$$\sim \mathcal{E}_{1s}^{\text{atom}} \tag{18}$$

[+] One can work out S_{12} for H_2 case and it has a sensitive dependence on separation R between two nuclei.

Important Remarks: Multi-center Integrals

$$S_{12} = \int \phi_{1s}^{*(L)}(\vec{r}-\vec{0})\,\phi_{1s}^{(R)}(\vec{r}-\vec{R})\,d^3r$$

different centers



may have region where both wavefunctions are not zero ⇒ $S_{12} \neq 0$ in general

* But $S_{12} = S_{12}(R) \to 0$ as R increases

Key idea

We will encounter multi-center integrals in LCAO and TBM

S_{12} is a two-center integral

Look at H_{11}, there is a term

$$\int \phi_{1s}^{*(L)}(\vec{r})\left[U_{atomic}(\vec{r}-\vec{0}) - \underbrace{V(\vec{r})}_{\underset{\text{from nucleus 1}}{U_{atom}(\vec{r})} + \underset{\text{from nucleus at } \vec{R}}{U_{atom}(\vec{r}-\vec{R})}}\right]\phi_{1s}^{(L)}(\vec{r})\,d^3r = -\int \phi_{1s}^{*(L)}(\vec{r})\,\overbrace{U_{atom}(\vec{r}-\vec{R})}^{\text{p.e. centered at } \vec{R} \text{ (LHS)}}\,\phi_{1s}^{(L)}(\vec{r})\,d^3r$$

$|\phi_{1s}^{(L)}(\vec{r})|^2$ ← centered at $\vec{0}$ (LHS)

$$-\int \underbrace{|\phi_{1s}^{(L)}(\vec{r})|^2 \, U_{atom}(\vec{r}-\vec{R})} \, d^3r$$

another two-center integral

interpretation: $\underbrace{(-e)|\phi_{1s}^{L}(\vec{r})|^2 d^3r}$

bit of electron's charge in 1s state on LHS atom sees "$U_{atom}(\vec{r}-\vec{R})$" the effect of the other nucleus

we claim that it is just a shift in the "on-site" energy

- Extension

× A   × B   × C   (3 centers)

possible to encounter $\int \phi_{1s}^{*(A)}(\vec{r}-\vec{R}_A) \, U_{atomic}(\vec{r}-\vec{R}_B) \, \phi_{1s}^{(C)}(\vec{r}-\vec{R}_C) \, d^3r$

A and C are Next-nearest neighbors

3-center integrals!

Harder NOT to be zero! 2-center integrals more important than 3-center integrals!

So, think "H_{11}" as an "on-site energy" related to the energy of the atomic AO to be involved in bonding

Empirical LCAO

- $\mathcal{E}_{nl}^{atom}$ values can be found in Tables!

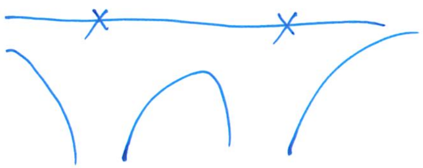
See Harrison, "Electronic Structure and the Properties of Solids" (developed LCAO and Empirical Tight-Binding Model into a rather simple calculation scheme with Tables to look up H_{ij} for different materials!

Similarly for H_{22}

H_{ij} : This is the part (terms in TISE) responsible for Bonding

$$\underset{\overset{\nearrow}{L}\ \overset{\uparrow}{R}}{H_{12}} = \int \underbrace{\phi_{1s}^{(L)}(\vec{r})}_{\text{centered at "}\vec{0}\text{"}} \ \hat{H} \ \underbrace{\phi_{1s}^{(R)}(\vec{r}-\vec{R})}_{\text{centered at } \vec{R}} \, d^3r$$

$\hat{H}$ ← include



Note: Exchange-type integrals (no classical interpretation) are involved in bonding! Quantum effect in Essence!

[illegible]

I am the electron. I can be on the LHS atom or RHS atom. The $\hat{H}$ in between includes the effect of the LHS nucleus if I am on the RHS [electron sees the effect of the presence of nearby atoms], and vice versa. This term promotes the spreading out of the electron to different sites. (19)

H_{12} (H_{ij}) is an energy (call it V_{12}) (or Δ_{12})

What is involved in H_{12}?

Among other terms, the important one is of the form

$$\int \phi_{1s}^{*(L)}(\vec{r})\; U_{atom}(\vec{r})\; \phi_{1s}^{(R)}(\vec{r}-\vec{R})\; d^3r$$

different centers

No classical interpretation

- important in determining energy gained by bonding
- sensitive to R

It is also a <u>two-center integral.</u>

It can be thought as the energy gained (promoting) for an electron to move from the RHS (at $\vec{R}$) site to the LHS (at $\vec{0}$) site and vice versa.

Then, for the example of both <u>atoms being</u> the <u>same</u> (like H_2), the Schrödinger Equation problem becomes

$$\begin{pmatrix} \varepsilon^{atom}-E & V_{12} \\ V_{12} & \varepsilon^{atom}-E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}=0$$

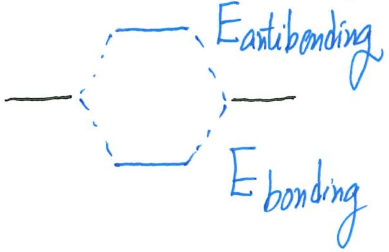
Note: V_{12} is often $\overbrace{\text{negative}}^{\text{for ss}\sigma\text{ bond}}$

$$\Rightarrow E_{bonding} = \varepsilon^{atom} - |V_{12}| \quad \left(= \varepsilon^{atom} + V_{12} \swarrow \text{itself negative} \right)$$

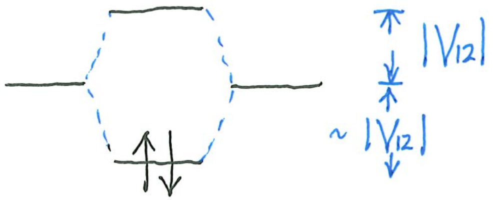
$$E_{antibonding} = \varepsilon^{atom} + |V_{12}| \quad \left(= \varepsilon^{atom} - V_{12} \right)$$

Isolated Atoms

Atoms at spacing appropriate for Bonding.



If each atom has 1 electron relevant to Bonding



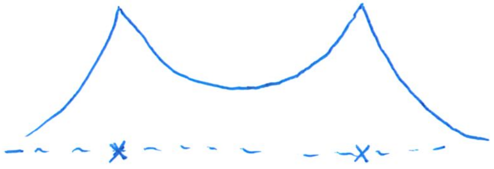
Energy Lowered by Forming Bond (thus from atoms to a molecule!)

$$\psi_{\text{bonding}} = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{(L)} + \phi_{1s}^{(R)}\right)$$

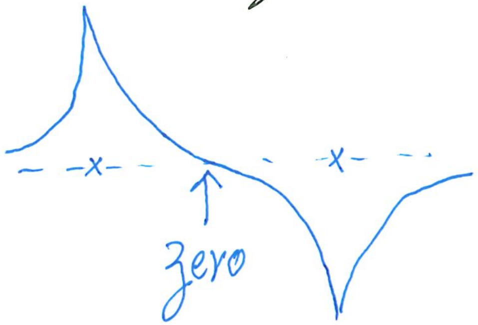
← same atoms ⇒ $|C_1| = |C_2|$

"$\frac{1}{\sqrt{2}}$" because assumed $S_{ij} = 0$

$$\psi_{\text{antibonding}} = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{(L)} - \phi_{1s}^{(R)}\right)$$



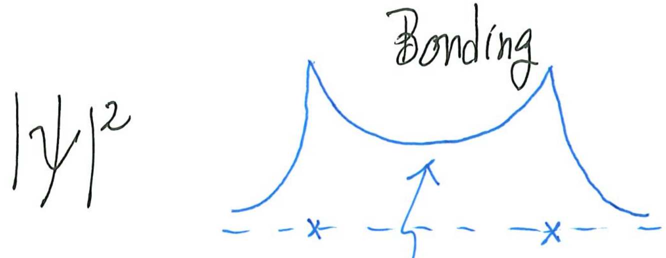
$\psi_{\text{bonding}} \sim \left(\phi_{1s}^{(L)} + \phi_{1s}^{(R)}\right)$



$\psi_{\text{antibonding}} \sim \left(\phi_{1s}^{(L)} - \phi_{1s}^{(R)}\right)$

The 2-electron state for both electrons in ψ_{bonding} is

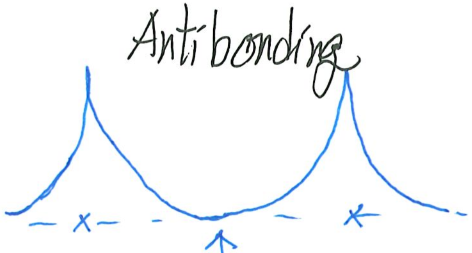
$$\Psi(1,2) = \psi_{\text{bonding}}(1)\,\psi_{\text{bonding}}(2)\cdot\underbrace{\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)}_{\text{spin part}}$$



enhanced probability between nuclei

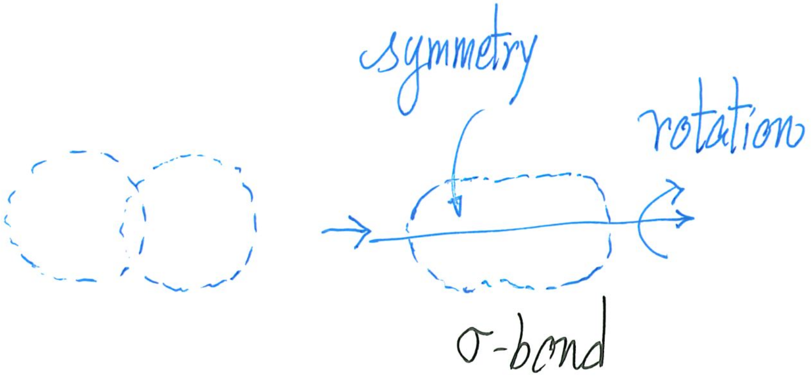
[Covalent Bond]

a consequence after QM wavefunction is found



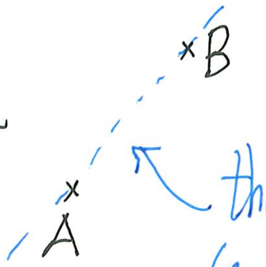
zero

This example is about ssσ bond.



Physical Insights

- Single atom → No idea of what $\hat{x}$, $\hat{y}$, $\hat{z}$ are about
- Two-atom ready for Bonding



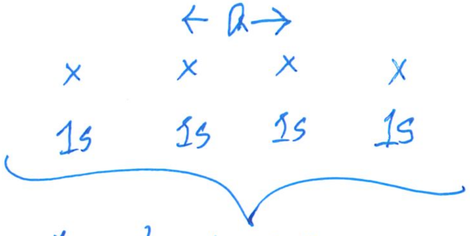
there is a special direction (call it $\hat{z}$ (OR $\hat{x}$, OR $\hat{y}$))

then p_z orbital has meaning

- Covalent or Ionic or Partially Covalent/Ionic is the answer of the TISE problem, given by the wavefunction ψ $(|\psi|^2)$.

- $|V_{12}|$ determines the range of energy between bonding and antibonding MO's.

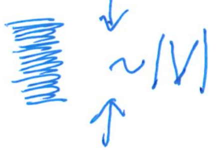
<u>What if 4 atoms?</u>



4 AO's LCAO
⇒ 4×4 problem ⇒ 4 MO's

But nearest neighboring H_{12}, H_{23}, H_{34} are more important

$$\begin{pmatrix} \varepsilon^{atom} & V & 0 & 0 \\ V & \varepsilon^{atom} & V & 0 \\ 0 & V & \varepsilon^{atom} & V \\ 0 & 0 & V & \varepsilon^{atom} \end{pmatrix} \Rightarrow \text{Eigenvalues?}$$

- Go into an array (a solid) ⇒ 

a band with <u>bandwidth</u> governed by |V|

LCAO is a very powerful way to consider the physics of electrons in solids

- Two different atoms? Many atoms (approach a solid)?
- Include More atomic orbitals from each atom?

A ×   B ×

$\phi^A_{1s}, \phi^A_{2s}, \phi^A_{2p_x, 2p_y, 2p_z}$ | $\phi^B_{1s}, \phi^B_{2s}, \phi^B_{2p_x, 2p_y, 2p_z}$

$\phi^A_{3s}, \phi^A_{3p_x, 3p_y, 3p_z}, \dots$ | $\phi^B_{3s}, \phi^B_{3p_x, 3p_y, 3p_z}, \dots$

$$\psi = \sum_i C^A_i \, \phi^A_i + \sum_j d^B_j \, \phi^B_j \qquad (20)$$

TISE ⇒ $n \times n$ matrix problem (n = total AO's used)

In principle, the more AO's, the better!

But a weak point of LCAO is that H_{ij} are <u>difficult to evaluate</u> from first principle!

Empirical H_{ij} treatment (Harrison^{+})

separation between nuclei (bond length)

$$H_{ij} \sim \frac{\hbar^2}{2m_e d^2} \quad (21) \qquad \boxed{\frac{\hbar^2}{m_e} = 7.62 \text{ eV-}\mathring{A}^2}$$

- this is an energy
- $\sim 1/d^2$ (closer ⇒ bigger V_{ij})

Harrison^{+}: $$H_{ij} = \eta \frac{\hbar^2}{2m_e d^2}$$

$^{+}$"Electronic Structure and the Properties of Solids"

η: a parameter (order 1), can be +ve/-ve

depends on type of bonding

$ss\sigma$, $sp\sigma$, $pp\sigma$, $pp\pi$

e.g. $\underbrace{\eta = -1.32 \quad 1.42 \quad 2.22 \quad -0.63}$

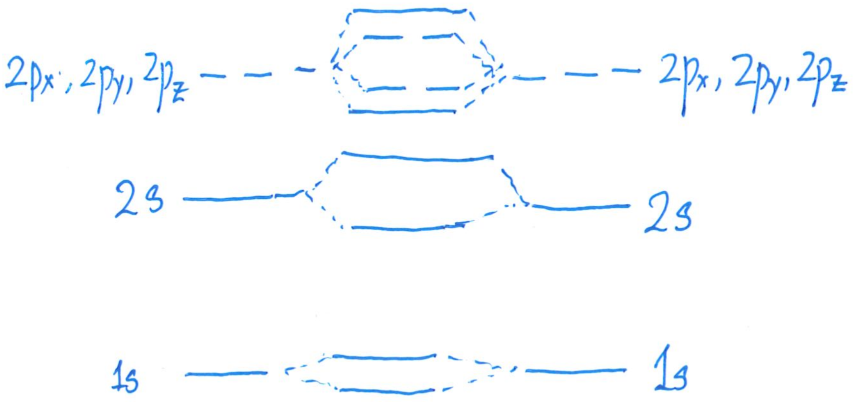
- obtained by fitting to many more accurate calculations
- transferable

Number of Molecular Orbitals (states) coming out equals the number of Atomic Orbitals involving in LCAO

A
(1s, 2s, $2p_x$, $2p_y$, $2p_z$)
[5]

B
(1s, 2s, $2p_x$, $2p_y$, $2p_z$)
[5]

Schematic

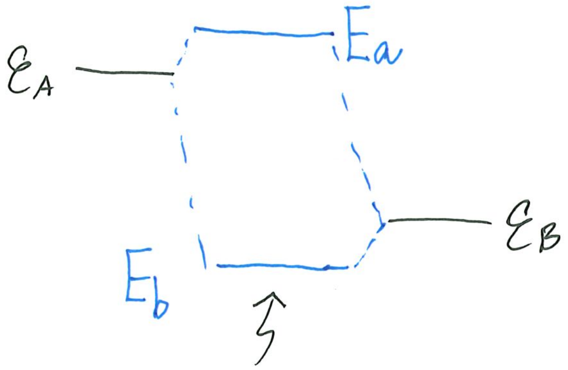


$$\underbrace{\underbrace{\text{10 AO's}}_{\text{linear combinations}}}_{\text{10 MO's}}$$

Diatomic Molecule with ionic character

AB molecule $(A \neq B)$

A contributes $\phi_s^{(A)}$, B contributes $\phi_{p_x}^{(B)}$



call it $\hat{x}$ direction

$$\begin{pmatrix} \varepsilon_A - E & V_{AB} \\ V_{AB} & \varepsilon_B - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\psi_{\text{bonding}} \approx \underbrace{(\text{big})\,\phi^{(B)}} + (\text{small})\,\phi^{(A)}$$

$$E_{\text{bonding}} = \frac{\varepsilon_A + \varepsilon_B}{2} - \sqrt{\left(\frac{\varepsilon_A - \varepsilon_B}{2}\right)^2 + V_{AB}^2} \approx \varepsilon_B - \frac{V_{AB}^2}{\varepsilon_A - \varepsilon_B}$$

$$E_{\text{antibonding}} = \frac{\varepsilon_A + \varepsilon_B}{2} + \sqrt{\left(\frac{\varepsilon_A - \varepsilon_B}{2}\right)^2 + V_{AB}^2} \approx \varepsilon_A + \frac{V_{AB}^2}{\varepsilon_A - \varepsilon_B}$$

ψ is bigger on the B-atom side

⇒ more electron charge appears on B-atom side

⇒ Ionic character $B \to B^-$, $A \to A^+$ to some extent

(c) sp, sp^2 Hybridization

LCAO

sp hybridization: Specific linear combination of s AO and p AO of the SAME ATOM when doing LCAO (to achieve more stable molecule)

"sp" Standard Examples: BeH_2 (it exists), C_2H_2 (it exists)

Be: $\underbrace{(1s^2)}_{\text{Core}}$ $\underbrace{2s^2}_{\text{full}}$ (shouldn't be chemically active)

But

Be: ϕ_{2s}^{Be} $\phi_{2p_x}^{Be}$ for LCAO

$H^{(L)}$: $\psi_H^{(L)}$ (1s)

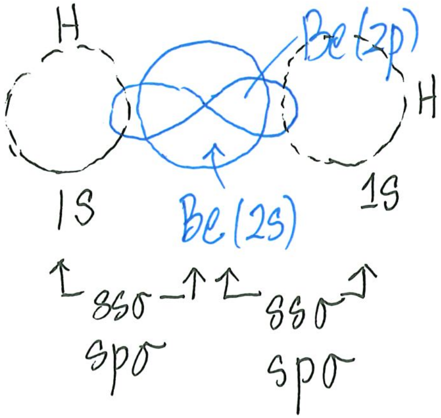
$H^{(R)}$: $\psi_H^{(R)}$ (1s)

4 AO's for LCAO

$$\psi = C_L \psi_H^{(L)} + C_{2s}^{Be}\phi_{2s}^{Be} + C_{2p}^{Be}\phi_{2p}^{Be} + C_R \psi_H^{(R)}$$

⇒ 4x4 matrix problem

With these 4 AO's, the eigenvalue problem is (schematically[†])



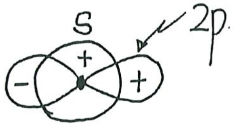
$$
\begin{array}{c|cccc}
 & \psi_H^{(L)} & \phi_{2s}^{Be} & \phi_{2p_x}^{Be} & \psi_H^{(R)} \\
\hline
\psi_H^{(L)} & \varepsilon_H & V_{ss\sigma} & V_{sp\sigma} & \approx 0 \\
\phi_{2s}^{Be} & V_{ss\sigma} & \varepsilon_{2s}^{Be} & \approx 0 & V_{ss\sigma} \\
\phi_{2p}^{Be} & -V_{sp\sigma} & \approx 0 & \varepsilon_{2p}^{Be} (\approx \varepsilon_{2s}^{Be}) & V_{sp\sigma} \\
\psi_H^{(R)} & \approx 0 & V_{ss\sigma} & -V_{sp\sigma} & \varepsilon_H
\end{array}
$$

- Many Non-zero off-diagonal elements
- Physically not transparent!
- Just find eigenvalues/eigenstates, fill in electrons, DONE!

[†] Don't worry about signs in some terms. Those are technical details.

$$\underbrace{\text{Matrix Equation}}_{\text{change basis}} \Leftrightarrow \underbrace{\text{simultaneous equations}}_{\text{multiply an equation by 2, say, and add to another equation}}$$

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

Be 

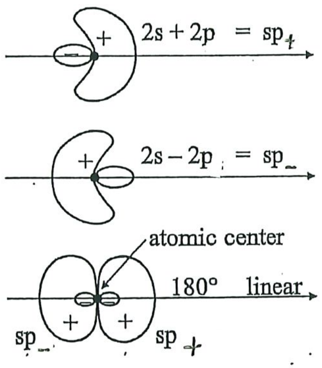
$$\begin{array}{c|cc} & \phi_{Be,2s} & \phi_{Be,2p} \\ \hline \phi_{Be,2s} & & \\ \phi_{Be,2p} & & \end{array}$$

<u>Advantageous to form linear combinations</u>: ["two in two out"]

sp hybridized states
$$\left\{ \begin{aligned} \psi^{(Be)}_{sp\,hybrid\,1} &= \frac{1}{\sqrt{2}}\left(\psi_{Be,2s} + \psi_{Be,2p}\right) \\ \psi^{(Be)}_{sp\,hybrid\,2} &= \frac{1}{\sqrt{2}}\left(\psi_{Be,2s} - \psi_{Be,2p}\right) \end{aligned} \right. \quad (21)$$

<u>same atom</u>

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



*

*

together

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

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

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

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

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

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

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

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

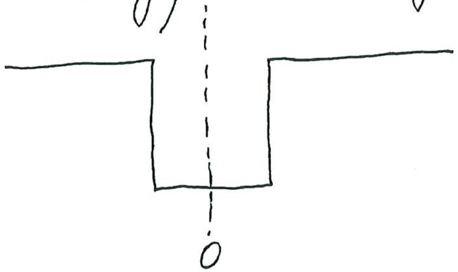
$\Rightarrow C_B = -\frac{\sqrt{2}}{2} = -\frac{1}{\sqrt{2}}$

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

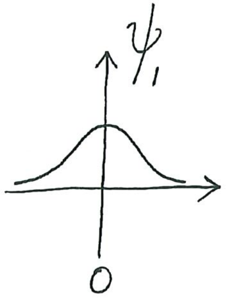
$\psi_A \sim +\psi_p$ (point at $+\hat{x}$ direction); $\psi_B \sim -\psi_p$ ($-\hat{x}$-direction) $\overbrace{(180^\circ \text{ apart})}^{\text{in physical space}}$

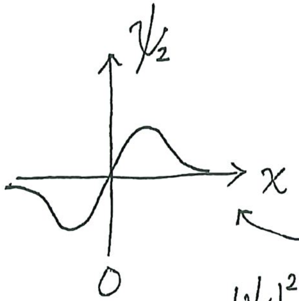
$\rightarrow \vec{V}_A$ $\boxed{\vec{V}_A \cdot \vec{V}_B = -1}$ $\vec{V}_B \leftarrow$

Analogy : 1D finite well



Ground state
(like s)





1st excited state
(like p)

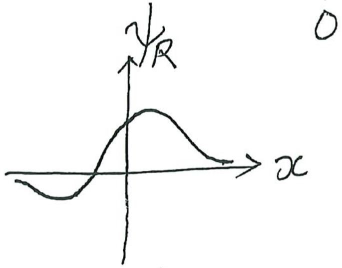
analogous to sp
hybrid orbitals

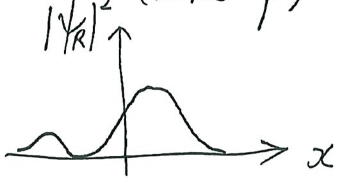
$$\psi_R \propto \psi_1 + \psi_2$$

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

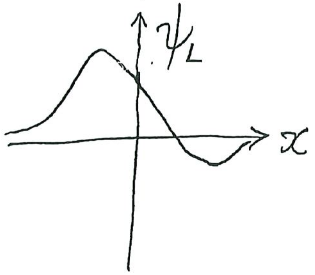
$$\psi_L \propto \psi_1 - \psi_2$$

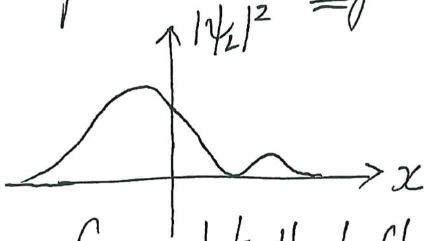
$[\text{like } \psi_s - \psi_p]$





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)

$$
\begin{array}{c|cccc}
 & & \swarrow \text{changed basis} & \searrow & \\
 & \psi_H^{(L)} & \psi_{\text{hybrid 1}}^{(Be)} & \psi_{\text{hybrid 2}}^{(Be)} & \psi_H^{(R)} \\
\hline
\psi_H^{(L)} & \varepsilon_H & \frac{1}{\sqrt{2}}(V_{ss\sigma}+V_{sp\sigma}) & \frac{1}{\sqrt{2}}(V_{ss\sigma}-V_{sp\sigma}) & 0 \\
\text{changed basis} \rightarrow \psi_{\text{Hybrid 1}}^{(Be)} & \frac{1}{\sqrt{2}}(V_{ss\sigma}+V_{sp\sigma}) & \frac{\varepsilon_{2s}^{Be}+\varepsilon_{2p}^{Be}}{2} & \sim\frac{\varepsilon_{2s}^{Be}-\varepsilon_{2p}^{Be}}{2} & \frac{1}{\sqrt{2}}(V_{ss\sigma}-V_{sp\sigma}) \\
\rightarrow \psi_{\text{Hybrid 2}}^{(Be)} & \frac{1}{\sqrt{2}}(V_{ss\sigma}-V_{sp\sigma}) & \sim\frac{\varepsilon_{2s}^{Be}-\varepsilon_{2p}^{Be}}{2} & \frac{\varepsilon_{2s}^{Be}+\varepsilon_{2p}^{Be}}{2} & \frac{1}{\sqrt{2}}(V_{ss\sigma}+V_{sp\sigma}) \\
\psi_H^{(R)} & 0 & \frac{1}{\sqrt{2}}(V_{ss\sigma}-V_{sp\sigma}) & \frac{1}{\sqrt{2}}(V_{ss\sigma}+V_{sp\sigma}) & \varepsilon_H
\end{array}
$$

(Schematic)

Now $\varepsilon_{2s}^{Be} \approx \varepsilon_{2p}^{Be}$; $V_{ss\sigma}+V_{sp\sigma}$ more important than $(V_{ss\sigma}-V_{sp\sigma})$ [say]

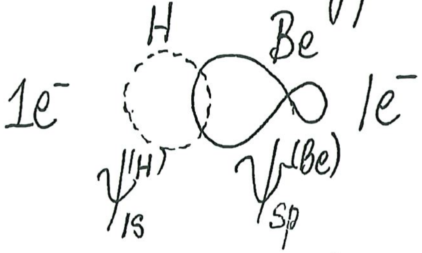
The Problem emerges as :

$$\begin{array}{c|cc|cc}
 & \psi_H^{(L)} & \psi_{hybrid1} & \psi_{hybrid2} & \psi_H^{(R)} \\ \hline
\psi_H^{(L)} & \varepsilon_H & V & \approx 0 & 0 \\
\psi_{hybrid1} & V & \frac{\varepsilon_{2s}^{Be}+\varepsilon_{2p}^{Be}}{2} & 0 & 0 \\ \hline
\psi_{hybrid2} & 0 & 0 & \frac{\varepsilon_{2s}^{Be}+\varepsilon_{2p}^{Be}}{2} & V \\
\psi_H^{(R)} & 0 & 0 & V & \varepsilon_H
\end{array}$$

Two (2x2) blocks

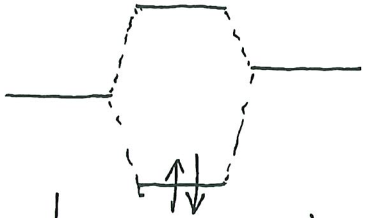
- This is more Physically Transparent!
- V is bigger than $V_{ss\sigma}$ and $V_{sp\sigma}$ alone ⇒ $\overbrace{\text{Stronger Pushing}}^{\text{Gain more energy}}$

Gain Energy by forming bonds (BeH_2)



$$\begin{array}{c|cc} & \psi_{H}^{(L)} & \psi_{sp\ hybrid}^{(Be)} \\ \hline \psi_{H}^{(L)} & \varepsilon_{1s}^{(H)} & V \\ \psi_{sp\ hybrid}^{(Be)} & V & \varepsilon_{hybrid}^{(Be)} \end{array}$$

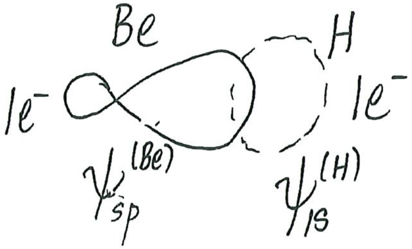
($|V|$ becomes bigger)



stronger pushing lowers energy

H — Be ···· H

this bond



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

($|V|$ becomes bigger)

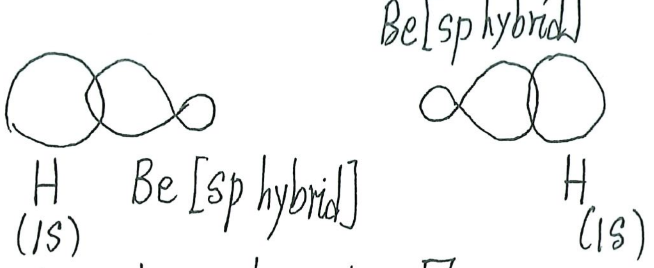
stronger pushing lowers energy

H ···· Be — H

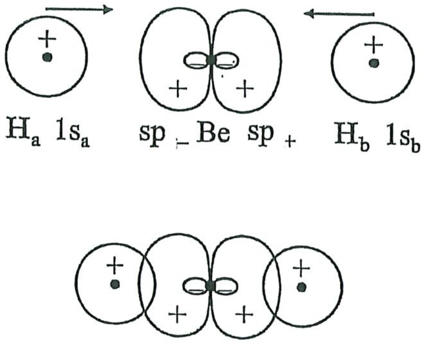
this bond

This is the QM story behind hybridization → focus wavefunction in directions
→ spread out to avoid Coulomb repulsion

Key Idea: It is a description of the QM approach based on LCAO



[Good overlap, strong bond]



BeH_2

[energy is lowered]

Ex. How about C_2H_2?

10 × 10 matrix problems!

$$H - C^{(L)} - C^{(R)} - H \ ?$$

$$\underbrace{1s}_{1} \quad \underbrace{2s, 2p_x\ (2p_y, 2p_z)}_{4} \quad \underbrace{2s, 2p_x\ (2p_y, 2p_z)}_{4} \quad \underbrace{1s}_{1}$$

(10 Atomic Orbitals)

Invoke $\frac{1}{\sqrt{2}}\left(\phi^{(L)}_{2s} \pm \phi^{(L)}_{2p_x}\right) = \psi^{L}_{sp1}, \psi^{L}_{sp2}$

$$\frac{1}{\sqrt{2}}\left(\phi^{(R)}_{2s} \pm \phi^{(R)}_{2p_x}\right) = \psi^{R}_{sp1}, \psi^{R}_{sp2}$$

10 × 10 becomes five (2×2 blocks) approximately.

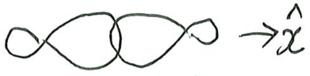
$H - C^{(L)}$;

1e⁻ from H

1e⁻ from $C^{(L)}$

fill Bonding Molecular Orbital

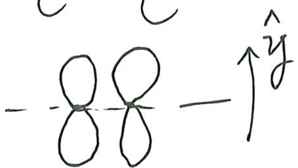
$C^{(L)} - C^{(R)}$;



Carbon-Carbon σ bond

$C^{(R)} - H$;

$C^{(L)} - C^{(R)}$;



π bond

$C^{(L)} - C^{(R)}$

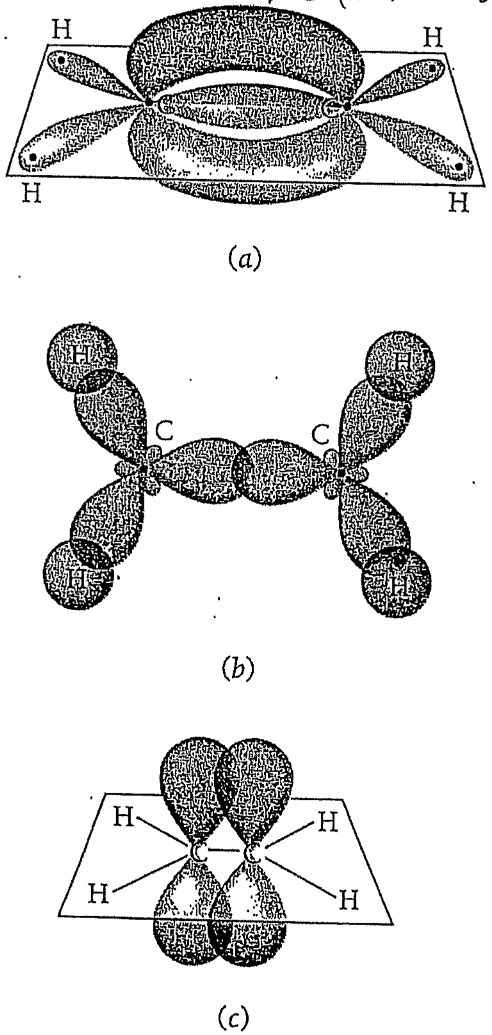
π bond

$$H - C \overset{}{\equiv} C - H$$

↑ triple bond

sp^2 Hybridization [C_2H_4 ethylene, Benzene's planar structure, graphene]

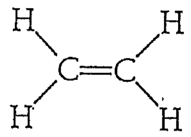
double (one σ and one π) bond



(*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.

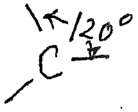
Top View

Ethylene



Again, highly directional

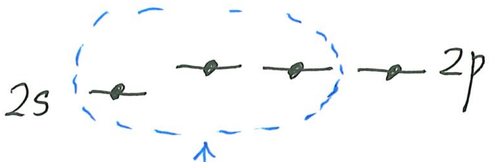
[120° between bonds.]



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

Same Physics - It is LCAO

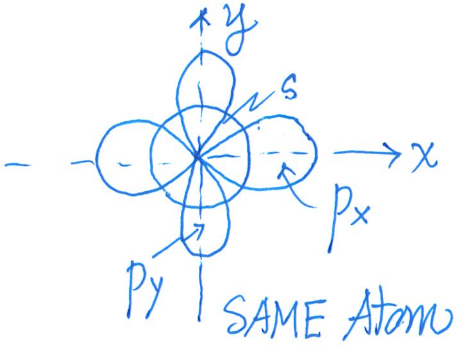
Carbon



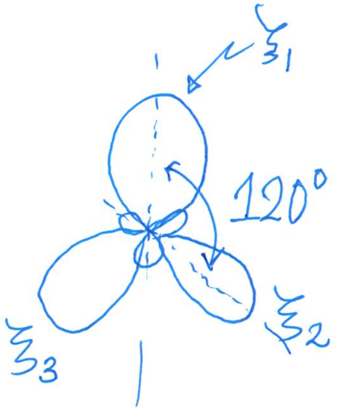
LCAO of AO's from SAME ATOM

⇒ prepare for forming stronger bonds

Take s, p_x, p_y



$$\begin{cases} \xi_1 = \frac{1}{\sqrt{3}}\left(\phi_{2s} + \sqrt{2}\,\phi_{2p_y}\right) \\ \xi_2 = \frac{1}{\sqrt{3}}\left(\phi_{2s} - \frac{1}{\sqrt{2}}\phi_{2p_y} + \sqrt{\frac{3}{2}}\,\phi_{2p_x}\right) \\ \xi_3 = \frac{1}{\sqrt{3}}\left(\phi_{2s} - \frac{1}{\sqrt{2}}\phi_{2p_y} - \sqrt{\frac{3}{2}}\,\phi_{2p_x}\right) \end{cases} \quad (22)$$



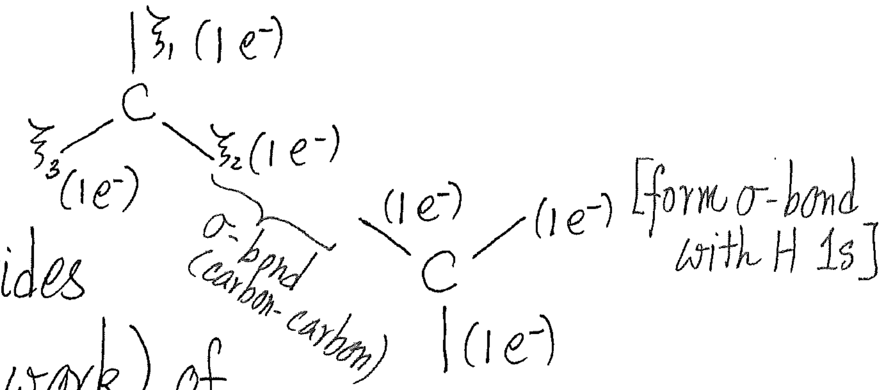
They are mutually orthogonal (check) and normalized.

These are the sp^2 Hybridized orbitals.

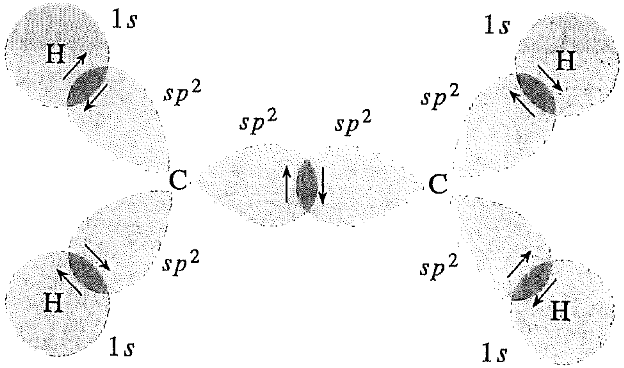
[There is still a $2p_z$ (out and into the plane) with one electron in it]

Consequences

- Plane of hybrid orbitals

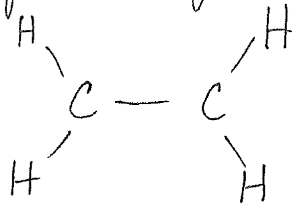


sp^2 hybridization provides the skelation (framework) of forming strong σ-bonds (direction) and dictates the structure



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

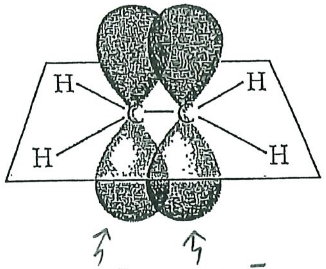
Rigid (strong)



Framework

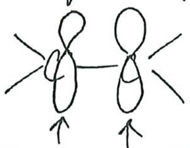
What's left?

Done! (from strong framework)



Quick QM thinking on π-bond

- After forming the strong σ-bonds skeleton



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

(LCAO, 2x2 matrix problem)

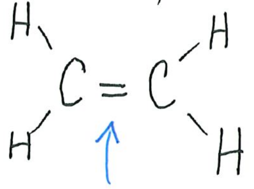
1e	1e
(2p)	(2p)
(left)	(right)

These electrons are called π electrons

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

π-bond (Done!)

Finally



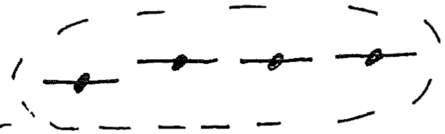
double bond (one σ; one π)

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.

(d) 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

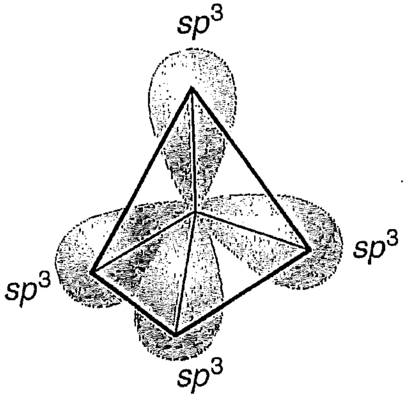
$$\psi_i = \frac{1}{\sqrt{4}}\psi_s + b_i \psi_{p_x} + c_i \psi_{p_y} + d_i \psi_{p_z} \qquad (23)$$

($i = 1, 2, 3, 4$) require ψ_i to be _normalized_ and _mutually orthogonal_

The end results are

$$\psi_1 = \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})$$
$$\psi_2 = \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})$$
$$\psi_3 = \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \qquad (24)$$
$$\psi_4 = \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})$$

sp^3 hybrid orbitals



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

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

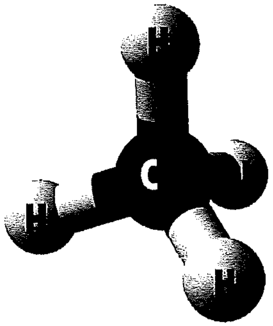
- Highly directional
- Like four vectors in

$$\left\{\begin{array}{ll} (+1,+1,+1) & [\hat{x}+\hat{y}+\hat{z}] \\ (-1,-1,+1) & [-\hat{x}-\hat{y}+\hat{z}] \\ (+1,-1,-1) & [\hat{x}-\hat{y}-\hat{z}] \\ (-1,+1,-1) & [-\hat{x}+\hat{y}-\hat{z}] \end{array}\right\}$$

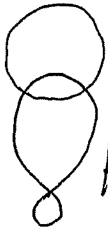
directions (OR rotated as a whole)

What for? To lower energy by forming bonds

Methane CH_4



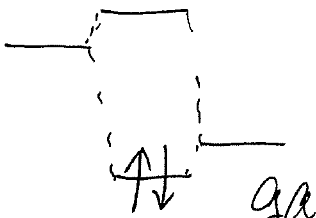
For each hybrid orbital (say ψ_i), there is one electron ready for bonding.



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

Δ is made bigger by

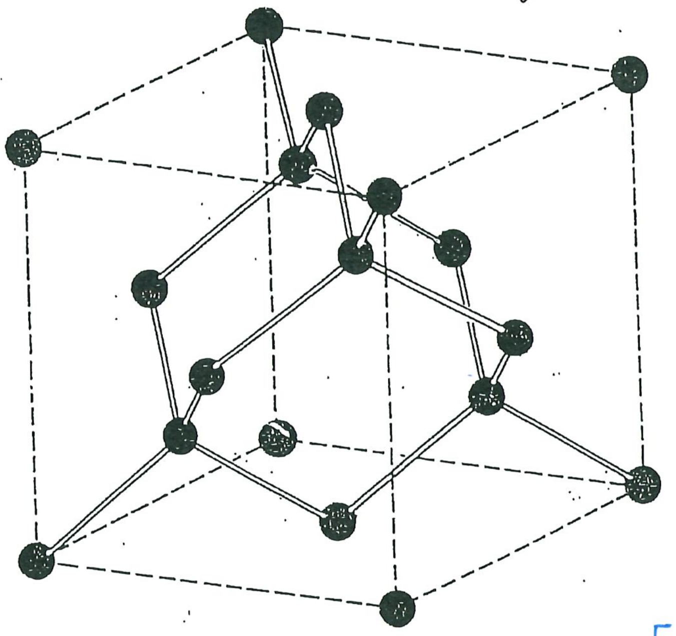
- Hybrid orbital focuses electron towards $\psi_{H,1s}$
- Hybrid orbitals spread electrons farther apart

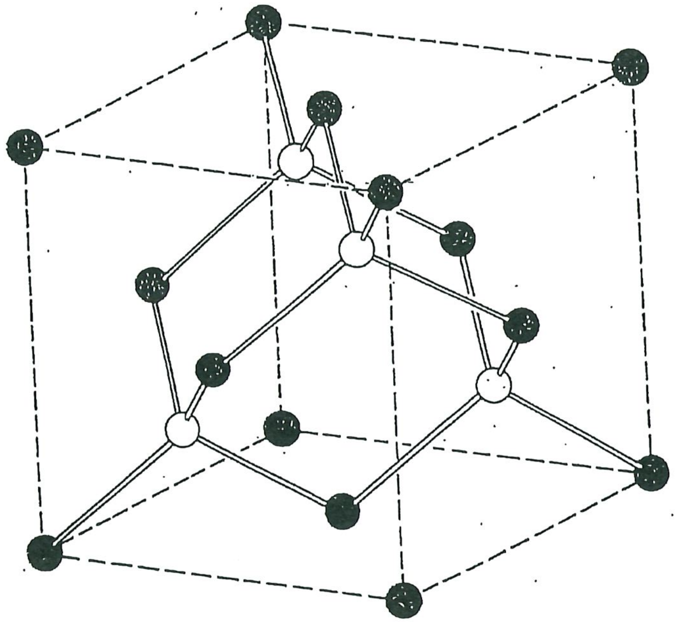


gain energy for each σ-bond formed

[Same physics works!]

sp^3 Hybridization governs most semiconductors' structure





Every atom : sp^3

Diamond Structure

- Same atom at every ●

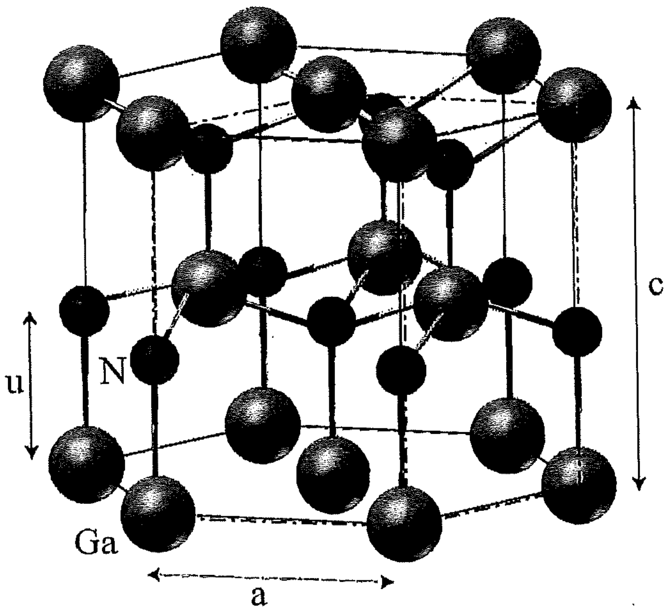
[e.g. carbon, silicon, germanium] ←

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.

Take-Home Messages

- LCAO (based on Turning QM TISE problem into a small-size Matrix Problem) provides a physically transparent way of understanding bonding and the physics of solids
- Hybridized orbitals are a picture emerged from QM treatment
- sp^3 involves linearly combining s, p_x, p_y, p_z (Si, Ge, ...), with the resulting hybridized orbitals from nearest neighboring atoms having strong matrix element ⇒ stronger pushing

the one pushed down (bonding)

fill in electrons (gain energy)

[This is what makes diamond a very strong material.]