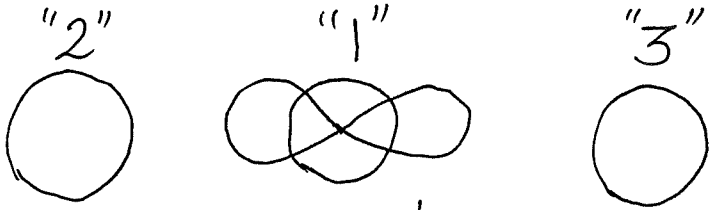
Appendix: Why bother†? How hybridization emerges from considering Bonding?

"Physical (Math) Picture" of hybridization

NOT Boron!

Consider "AB_2" molecule (3 atoms: One "A", two "B"'s)



(4 atomic orbitals are involved)

	B	A	B
	s	s and p	s
	1 electron available for bonding	2 electrons available for bonding	1 electron available for bonding

For atom A, let's say ε_s and ε_p are close enough ⇒ not much energy to put an electron in p (another in s)

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† This is a conceptually challenging appendix, although non-mathematically. Values in Matrices are meant to be schematic.

LCAO: $\underbrace{|1\rangle \equiv |A,s\rangle, |2\rangle \equiv |A,p\rangle}_{\text{from A atom}}$; $|3\rangle \equiv \underbrace{|L,s\rangle}_{\text{Left atom's s AO}}$; $|4\rangle \equiv \underbrace{|R,s\rangle}_{\text{Right atom's s AO}}$

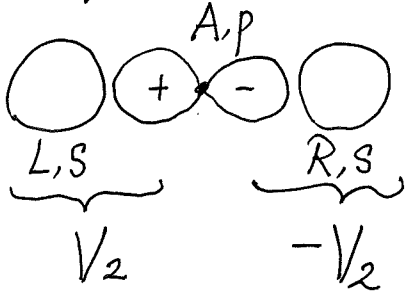
LCAO $\Rightarrow$ 4×4 matrix eigenvalue problem

		Atom A		Left B	Right B
		$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$
Atom A	$\langle 1\|$	ε_s	≈ 0	V_1	V_1
Atom A	$\langle 2\|$	≈ 0	$\varepsilon_p \approx \varepsilon_s$	V_2	$-V_2$
Left B	$\langle 3\|$	V_1	V_2	$\varepsilon_{B,s}$	≈ 0
Right B	$\langle 4\|$	V_1	$-V_2$	≈ 0	$\varepsilon_{B,s}$

(A1)

V_1: How $\hat{H}$ connects $|A,s\rangle$ to left and right atoms' s AO's.

V_2: How $\hat{H}$ connects $|A,p\rangle$ to left and right atoms' s AO's



$$H_{ij} = \int \psi_i^* \hat{H}_{el}^{(molecule)} \psi_j \, d\tau$$

- Could solve (A1) for eigenvalues ⇒ MO's energies
  eigenstates ⇒ MO's wavefunctions

Done! [No idea (no need to invoke idea) on hybridization!]

- What if we manipulate the matrix by adding/substracting rows/columns? or <u>changing basis</u>?
  - Will not affect eigenvalues
- Write (A1) in new basis?

$$\text{(A2)}\begin{cases} |+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) = \frac{1}{\sqrt{2}}(|A,s\rangle + |A,p\rangle) \\ |-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) = \frac{1}{\sqrt{2}}(|A,s\rangle - |A,p\rangle) \end{cases}$$

sp hybrid orbitals in A atom

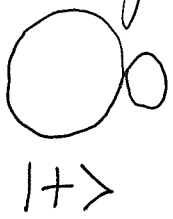
Use $|+\rangle$, $|-\rangle$, $\underbrace{|3\rangle}_{\text{Left}}$, $\underbrace{|4\rangle}_{\text{Right}}$ as new basis

	A atom: Hybrid orbitals $\lvert+\rangle$	$\lvert-\rangle$	Left B $\lvert3\rangle$	Right B $\lvert4\rangle$
Hybrid orbitals $\langle+\rvert$	ε	0	V_1+V_2	V_1-V_2
Hybrid orbitals $\langle-\rvert$	0	ε	V_1-V_2	V_1+V_2
Left B $\langle3\rvert$	V_1+V_2	V_1-V_2	$\varepsilon_{B,S}$	0
Right B $\langle4\rvert$	V_1-V_2	V_1+V_2	0	$\varepsilon_{B,S}$

(A3)

Started to see $\lvert+\rangle$ interacts stronger (weaker) with $\lvert3\rangle$ ($\lvert4\rangle$)

"pointing" to left $\lvert-\rangle$ interacts stronger (weaker) with $\lvert4\rangle$ ($\lvert3\rangle$)



$\lvert+\rangle$

- Let's assume $V_1 \approx V_2$ so that $V_1 - V_2 \approx 0$. Eq. (A3) becomes

$$\begin{array}{c} \\ \langle + | \\ \langle - | \\ \langle 3 | \\ \langle 4 | \end{array} \begin{array}{c} \begin{array}{cccc} |+\rangle & |-\rangle & |3\rangle & |4\rangle \end{array} \\ \begin{pmatrix} \varepsilon & 0 & V & 0 \\ 0 & \varepsilon & 0 & V \\ V & 0 & \varepsilon_{B,S} & 0 \\ 0 & V & 0 & \varepsilon_{B,S} \end{pmatrix} \end{array} \qquad \text{(A4)}$$

[Write $V_1 + V_2 = V$]

Done!

- $|+\rangle$ and $|3\rangle$ interact (to form bonding/anti-bonding MO's)
- $|-\rangle$ and $|4\rangle$ interact (to form bonding/anti-bonding MO's)

[clear physical picture emerges]

- Rearranging rows and columns

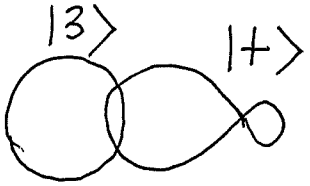
$$\begin{array}{c} \\ \langle + | \\ \langle 3 | \\ \langle - | \\ \langle 4 | \end{array} \begin{array}{c} \begin{array}{cccc} |+\rangle & |3\rangle & |-\rangle & |4\rangle \end{array} \\ \left(\begin{array}{cc:cc} \mathcal{E} & V & 0 & 0 \\ V & \mathcal{E}_{B,S} & 0 & 0 \\ \hdashline 0 & 0 & \mathcal{E} & V \\ 0 & 0 & V & \mathcal{E}_{B,S} \end{array}\right) \end{array} \qquad (A5)$$

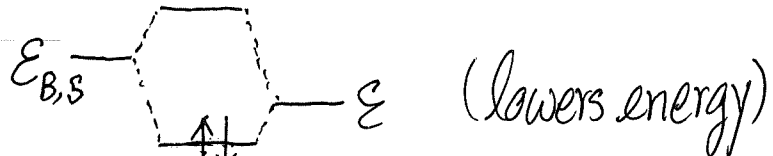
Equivalent to Eq. (A4)

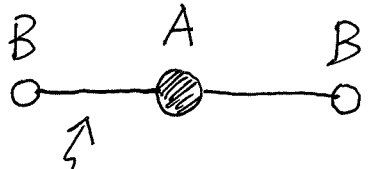
- Clearly becomes two 2x2 blocks

(Left B)

$$\begin{array}{c} \\ \langle + | \\ \langle 3 | \end{array} \begin{array}{c} \begin{array}{cc} |+\rangle & |3\rangle \end{array} \\ \begin{pmatrix} \varepsilon & V \\ V & \varepsilon_{B,S} \end{pmatrix} \end{array}$$

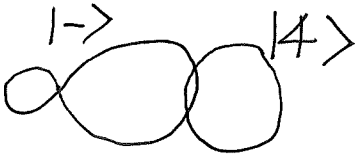


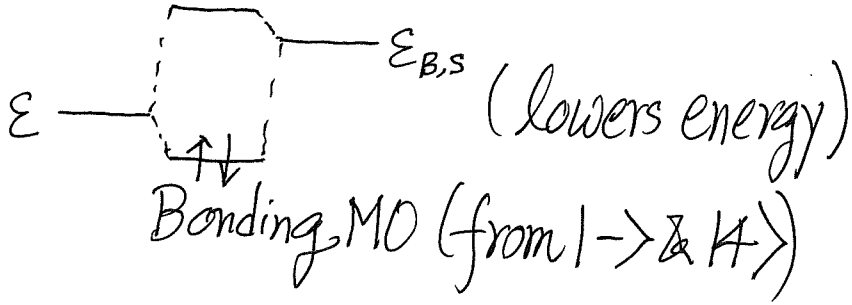


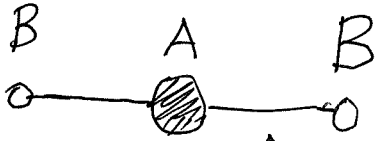


giving this bond

$$\begin{array}{c} \\ \langle - | \\ \langle 4 | \end{array} \begin{array}{c} \begin{array}{cc} |-\rangle & |4\rangle \end{array} \\ \begin{pmatrix} \varepsilon & V \\ V & \varepsilon_{B,S} \end{pmatrix} \end{array}$$



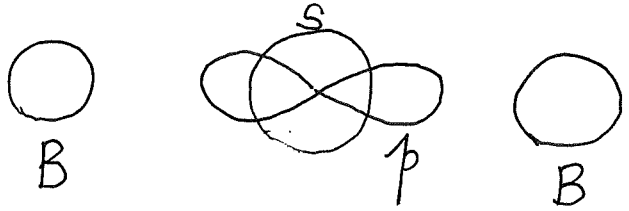


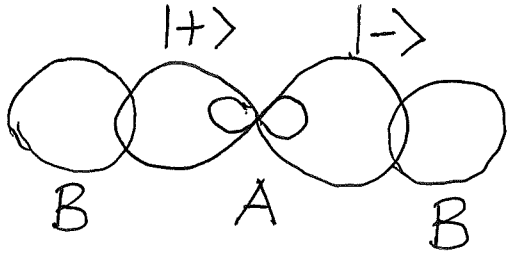


giving this bond

Same strength: each makes good use of |A,s⟩, |A,p⟩ interaction with B atoms s.

This is the <u>Quantum Mechanics</u> behind the scenario of hybridization and how hybrid orbitals help form strong and directional bonds.





A way to describe the Quantum Mechanics of Bond Formation
(the results of the QM problem)
in a clever and clear picture!

Take-Home Messages

- LCAO : can include several AO's from each atom
- Under suitable conditions (BeH_2, benzene, CH_4, diamond, ...), bonding (QM results) can be described by first forming hybrid orbitals by combining AO's of the same atom and then using hybrid orbitals to form MO's with other atoms.
- It is just a way to describe the QM results!

—End of Appendix—