

Lecture 1 CH102 A2 (MWF 11:15 am) Spring 2018 Copyright © 2018 Dan Dill dan@bu.edu

[TP] Based on the correlation diagrams, what is true about the relative polarity of the molecules WX, WY, and XY?

20% 1. WY is more polar than XY  
 20% 2. WX is more polar than XY  
 20% 3. 1 and 2  
 20% 4. Neither 1 nor 2  
 20% 5. Further information needed

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Lecture 1 CH102 A2 (MWF 11:15 am)  
 Friday, January 19, 2018

- When atoms are different, which AOs combine to make MOs? "Bonding in diatomic molecules," <https://goo.gl/1h0S9C>
- Use Symmetry, Overlap, Energy (SOE) to decide which AOs combine "Questions on Symmetry, Overlap, Energy," <http://goo.gl/oYEF3b>

Next: MO description of hydroxide, OH<sup>-</sup>; MO description of water; Begin "Hybrid AOs and Polyatomic MOs," <http://goo.gl/6hBD8X>  
 Ethane, H<sub>3</sub>C-CH<sub>3</sub>

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### When atoms are different, which AOs combine?

SOE: Symmetry, Overlap, Energy

- Symmetry:** Which AOs have nonzero overlap?
- Overlap:** Which AOs combine with the greatest bonding/antibonding effect?
- Energy:** How does relative AO energy affect composition of MOs?

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### When atoms are different, which AOs combine?

They must have the correct **symmetry**.

OK example:  $2s + 2p_z$   
 (z is bond axis)

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## When atoms are different, which AOs combine?

They must have the correct **symmetry**.

Not OK example:  $2s + 2p_x$   
( $x$  is perpendicular to bond axis)



9

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## When atoms are different, which AOs combine?

They must have appreciable **overlap**.

Orbital size is  $\approx 50 \text{ pm } n^2 / Z_{\text{eff}}$

What are  $n$  and  $Z_{\text{eff}}$  for Li 1s?

What are  $n$  and  $Z_{\text{eff}}$  for Li 2s?

	$n$	$Z_{\text{eff}}$	Orbital size
Li 1s	1	3	$(1/3) 50 \text{ pm} = 17 \text{ pm}$
Li 2s	2	1.2	$(4/1.2) 50 \text{ pm} = 170 \text{ pm}$



11

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## When atoms are different, which AOs combine?

They must have appreciable **overlap**.

Orbital size is  $\approx 50 \text{ pm } n^2 / Z_{\text{eff}}$

This means **only valence AOs**, ...

because the inner-shell AO's are **too small**, ...

because of their **larger  $Z_{\text{eff}}$**  and **smaller  $n$** .



12

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## 1s clouds much smaller than 2s clouds

<http://quantum.bu.edu/CDF/101/Li2Bonding1sAnd2sElectronClouds.cdf>



14

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### 1s clouds much smaller than 2s clouds

<http://quantum.bu.edu/CDF/101/Li2Bonding1sAnd2sElectronClouds.cdf>

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15

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### At maximum 2s bonding ( $R = R_e$ ), no 1s bonding

<http://quantum.bu.edu/CDF/101/Li2Bonding1sAnd2sElectronClouds.cdf>

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16

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### At maximum 2s antibonding, no 1s antibonding

<http://quantum.bu.edu/CDF/101/Li2Antibonding1sAnd2sElectronClouds.cdf>

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17

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### When atoms are different, which AOs combine?

They must have appreciable **overlap**.

OK example: 2s + 2s

Not OK example: 1s + 1s

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### Only valence AO's affect bonding/antibonding

Here is the correlation diagram we have seen for  $\text{Li}_2$  (fig 10.22, p 402).

Sketch a more correct version.

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### When atoms are different, which AOs combine?

They must be close in **energy**.

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20

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### Energy: Closer the better

<http://quantum.bu.edu/CDF/102/CorrDiagXY2s.cdf>

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24

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### Energy: Closer the better

<http://quantum.bu.edu/CDF/102/CorrDiagBondingXY2s.cdf>

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### Energy: Closer the better

Increasing energy

s orbital on less electronegative element

s orbital on more electronegative element

combine out-of-phase

combine in-phase

$\sigma^*$

$\sigma$

molecular orbitals from elements of different electronegativity

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27

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### Energy: Closer the better

Energies of AOs both the same

AD on atom B is a little lower in energy than AD on atom A

AD on atom B is a lot lower in energy than AD on atom A

large interaction between AOs

less interaction between AOs

ADs are too far apart in energy to interact

bonding MO much lower in energy than AOs

bonding MO is lowered only by a small amount relative to AD on atom B

the filled orbital on the atom has the same energy as the AD on atom B

antibonding MO is much higher in the energy than the AOs

antibonding MO is raised in energy by only a small amount relative to AD on atom B

the empty orbital on the atom has same energy as the AD on atom A

both AOs contribute equally to the MOs

electrons in bonding MO are shared equally between the two atoms

both AOs contribute more to the bonding MO and the AD on A

electrons in bonding MO are shared between atoms but are associated more with atom B than A

only one AO contributes to each MO

electrons in the filled orbital are located only on atom B

bond between A and B would classically be described as purely covalent

bond between A and B is covalent but there is also some electrostatic (ionic) attraction between atoms

bond between A and B would classically be described as purely ionic

antioxidant to break bond into two radicals

antioxidant to break bond into two ions, A<sup>+</sup> and B<sup>-</sup>, although it is also possible to give two radicals

comprand already exists as ions A<sup>+</sup> and B<sup>-</sup>

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28

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0% 2. WX is more polar than XY

0% 3. 1 and 2

0% 4. Neither 1 nor 2

0% 5. Further information needed

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29

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### Energy: Closer the better

<http://quantum.bu.edu/CDF/102/CorrDiagBondingXY2s.cdf>

So, WX is more polar than XY

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30

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[TP] Assume  $AO_1$  and  $AO_2$  have correct relative symmetry, greatest overlap, and are closest in energy.  $AO_1$  has  $IE = 5 \text{ eV}$  and  $AO_2$  has  $IE = 6 \text{ eV}$ . Which of the following is true?

- 0% 1. Bonding MO has more  $AO_1$  than  $AO_2$   
 0% 2. Bonding MO has more  $AO_2$  than  $AO_1$   
 0% 3. Antibonding MO is almost entirely  $AO_1$   
 0% 4. Antibonding MO is almost entirely  $AO_2$   
 0% 5. 1 and 4  
 0% 6. I do not know how to tell.

