

Lecture 2 CH102 A2 (MWF 11:15 am) Spring 2018 Copyright © 2018 Dan Dill dan@bu.edu

**[TP]** Which molecule has stronger covalent bonding?

33% 1. XH  
33% 2. YH  
33% 3. They are equal

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Lecture 2 CH102 A2 (MWF 11:15 am)  
Monday, January 22, 2018

- Covalent versus ionic character
- MO description of hydroxide, OH<sup>-</sup>
- MO description of water

**Next:** Accounting for molecular shape: Hybrid AOs; Water again: Hybrid AO-MO description; Polyatomic MO recipe: Formaldehyde, H<sub>2</sub>CO (localized  $\pi$  bond)

"Hybrid AOs and Polyatomic MOs," <http://goo.gl/6hBD8X> ;

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## Practice

Questions on Symmetry, Overlap, Energy  
<http://goo.gl/oYEF3b>

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**[Quiz]** Atom X has  $IE_1 = 17 \text{ eV}$  and atom Y has  $IE_1 = 12 \text{ eV}$ . Compared to molecule X:H, ...

- 0% 1. molecule Y:H has a **greater** dipole moment
- 0% 2. molecule Y:H has **the same** dipole moment
- 0% 3. molecule Y:H has a **smaller** dipole moment
- 0% 4. Neither molecule is polar
- 0% 5. Cannot know relative polarity without knowing the electronegativities of atoms H, X, and Y.

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### Covalent versus ionic character

Atom X has  $IE_1 = 17 \text{ eV}$ , atom Y has  $IE_1 = 12 \text{ eV}$ , and H has  $IE_1 = 13.6 \text{ eV}$ .

Since the ionization energies of X:H differ more than those of Y:H, ...

X:H has a **larger dipole moment** than Y:H.

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[TP] Which molecule has a **stronger covalent bonding**?

33% 1. XH  
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### Covalent versus ionic character

The charge shift results in the contribution  $\frac{\delta^- e \times \delta^+ e}{4\pi\epsilon_0 R_e}$  to the bond strength.

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### Covalent versus ionic character

The charge shift results in the contribution  $\frac{\delta^- e \times \delta^+ e}{4\pi\epsilon_0 R_e}$  to the bond strength.

While XH has **smaller covalent** bond effect, its larger charge shift means it has a **larger ionic** contribution to the bonding,

$$\left| \frac{\delta^- e \times \delta^+ e}{4\pi\epsilon_0 R_e} \right| = \left| -\frac{0.70^2 e^2}{4\pi\epsilon_0 R_e} \right| > \left| -\frac{0.21^2 e^2}{4\pi\epsilon_0 R_e} \right|$$

For this reason, we say XH has **more ionic** character than YH

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MO description of water

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Sketch the AO-MO correlation diagram of HO<sup>-</sup>

Note:  $IE_O > IE_H$

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Sketch the AO-MO correlation diagram of HO<sup>-</sup>

Note:  $IE_O > IE_H$

The diagram shows the energy levels for the HO<sup>-</sup> molecule. On the left, the 1s orbital is at a high energy level with two electrons. On the right, the 2s orbital is at a lower energy level than the 1s orbital, with two electrons. The 2p orbitals (2p<sub>yz</sub> and 2p<sub>x,yz</sub>) are at an energy level between the 1s and 2s orbitals, with four electrons. The bonding molecular orbitals are  $\sigma_x$  and  $\sigma_x^*$ . The  $\sigma_x$  orbital is lower in energy than the 2s orbital, and the  $\sigma_x^*$  orbital is higher in energy than the 2p orbitals. Dashed lines indicate the correlation between the atomic orbitals and the molecular orbitals.

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Sketch the AO-MO correlation diagram of HO<sup>-</sup>

Why is the O 2s AO nonbonding?

This diagram is identical to the one in slide 15, but it includes the question "Why is the O 2s AO nonbonding?" to prompt a discussion about the energy mismatch between the oxygen 2s orbital and the hydrogen 1s orbital.

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**[TP]** In the  $\text{HO}^-$  correlation diagram, the O 2s AO is nonbonding because ...

0% 1. it has no net overlap with the H 1s AO  
 0% 2. It has the wrong symmetry  
 0% 3. it has a lower ionization energy than the O 2p AOs  
 0% 4. it has a larger  $Z_{\text{eff}}$  than the O 2p AOs

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### Sketch the AO-MO correlation diagram of $\text{HO}^-$

Why are two of the O 2p AOs nonbonding?

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**[Quiz]** In the  $\text{HO}^-$  correlation diagram, the two O 2p AOs are nonbonding because ...

25% 1. they have no net overlap with the H 1s AO  
 25% 2. they have a higher ionization energy than the H 1s AO  
 25% 3. they have a larger  $Z_{\text{eff}}$  than the H 1s AO  
 25% 4. 2 and 3

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Response Counter

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### Sketch the AO-MO correlation diagram of $\text{HOH}$

Hint: Represent the second H as an additional 1s AO

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