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[TP] Atom X have  $IE_X = 13 \text{ eV}$  and atom Y has  $IE_Y = 15 \text{ eV}$ .  
Compared to molecule X:H, ...

20% 1. molecule Y:H has a **greater** dipole moment  
20% 2. molecule Y:H has **the same** dipole moment  
20% 3. molecule Y:H has a **smaller** dipole moment  
20% 4. Neither molecule is polar  
20% 5. Cannot know relative polarity without knowing the electronegativities of atoms H, X, and Y.

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Friday, January 20, 2017

- Review: When atoms are different, which AOs make MOs
- Which AO's combine: Symmetry, overlap, energy
- MO description of hydroxide,  $\text{OH}^-$

Next: Continue "Hybrid AOs and Polyatomic MOs", <http://goo.gl/6hBD8X> :  
MO description of water. Hybrid AOs. Hybrid AO-MO description of water.  
Ethane,  $\text{H}_3\text{C}-\text{CH}_3$

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

AOs that have net overlap .

This always means **only valence AOs**,  
because the inner-shell AOs are too small,  
because of their much larger  $Z_{\text{eff}}$  (electron cloud very small)

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### Orbital size and shielding

When there is more than one electron, the one-electron-atom energy formula can be generalized to

$$\text{Orbital energy} = -13.6 \text{ eV } Z_{\text{eff}}^2 / n^2$$

where  $Z_{\text{eff}}$  is the **effective nuclear charge**.

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## Orbital size and shielding

The approximate size of the orbital is

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

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## Orbital size and shielding

The ionization energy of the orbital is

$$\begin{aligned} IE_{\text{orbital}} &= E_{\infty} - (-13.6 \text{ eV } Z_{\text{eff}}^2 / n^2) \\ &= 0 + 13.6 \text{ eV } Z_{\text{eff}}^2 / n^2 \\ &= 13.6 \text{ eV } Z_{\text{eff}}^2 / n^2 \end{aligned}$$

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## 1s clouds much smaller than 2s clouds

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

Li bonding 1s and 2s electron clouds

Separation

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

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

Li bonding 1s and 2s electron clouds

Separation

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

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

Li antibonding 1s and 2s electron clouds

Separation

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### Only valence AOs effect bonding/antibonding

<http://quantum.bu.edu/CDF/101/Li2BondingAndAntibonding2sElectronClouds.cdf>

Li bonding and antibonding 2s electron clouds

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### Only valence AOs effect bonding/antibonding

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

Energy

atomic orbitals

molecular orbitals

Sketch a more correct version.

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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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### Symmetry: Net overlap or not?

- For a pair of AO's to give a (bonding/antibonding) pair of MO's, there must be **net overlap** (net in-phase or net out-of-phase).
- If in-phase and out of phase overlap **exactly cancel**, the AO's remain uncombined, as **nonbonding orbitals**.



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### Overlap: Greater the better

- The more net overlap, the greater the bonding/antibonding effect.
- Core AO's have least negligible overlap, so ignore
- Only valence AO's have significant overlap



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### Energy: Closer the better

- The **closer** AO's are in energy, the **greater** the bonding/antibonding effect.
- If AO's have **same energy** (identical atoms, homonuclear bond), MO's will be **50% of each AO**.
- If AO's have **different energy** (different atoms, heteronuclear bond), ...
  - Bonding MO → contains more of the lower energy AO
  - Antibonding MO → contains more of the higher energy AO



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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

molecular orbitals from elements of different electronegativity

$\sigma^*$

$\sigma$

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### Energy: Closer the better

Energies of AOs both the same

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

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

large interaction between AOs

less interaction between AOs

AOs 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 AO on atom B

the filled orbital on the anion has the same energy as the AO 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 AO on atom B

the empty orbital on the cation has same energy as the AO on atom A

both AOs contribute equally to the MOs

electrons in bonding MO are shared equally between the two atoms

the AO on B contributes more to the bonding MO and the AO on A

electrons in the filled orbital are located only on atom B

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

electrons in the filled orbital are associated 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

resistant to break bond into two ions,  $A^+$  and  $B^-$ , although it is also possible to give two radicals

component already exists as ions  $A^+$  and  $B^-$

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### MO description of water

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### Sketch the AO-MO correlation diagram of $HO^-$

Note:  $IE_0 > IE_H$

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