

Lecture 36 CH101 A2 (MWF 11:15 am) Fall 2017 Copyright © 2017 Dan Dill dan@bu.edu

[TP] The decrease in IE_1 from Be to B primarily is due to ...

Element	IE ₁ (kJ/mol)
H	1312
He	2372
Li	520
Be	900
B	801
C	1086
N	1402
O	1314
F	1681
Ne	2081
Na	496

20% 1. increase in atom size
 20% 2. increase in the number of loops in the atomic orbitals
 20% 3. increase in electrical shielding
 20% 4. increase in effective nuclear charge
 20% 5. some other reason

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 Friday, December 8, 2017

For today ...

- Complete: Building electron configurations

Begin ch 10: Modeling bonding in molecules: <http://goo.gl/1h0S9C>

- Mixing atomic orbitals (AO's) makes molecular orbitals (MO's)
- 1s MO's: CDF <https://goo.gl/eliM2a>

Next lecture: AO-MO correlation diagrams; Bond order: H_2^+ to Be_2 (!);
 2p MO's: CDF <https://goo.gl/2MEiRA> ; B_2 to Ne_2

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C $2p_x^2$ or $2p_x 2p_y$?

$2p_x^2$ are in **same orbital** and so must have **greater** electron-electron **repulsion**

What about electrons in different 2p orbitals?

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Energy order of relative spins (Pauli)

Key point: "spin" = **magnetic moment**, either up or down

$\uparrow\uparrow$ impossible; $\uparrow\downarrow$ (**worst**) > $\uparrow \dots \downarrow$ > $\uparrow \dots \uparrow$ (**best**)

$\uparrow\downarrow$ (**worst**): Electrons in **same spatial region** (orbital) and so **repel** one another **the most**

$\uparrow \dots \downarrow$: Electrons **clump** together (**Fermi clump**) in **different spatial regions** (orbitals) and so **repel somewhat less**

$\uparrow \dots \uparrow$ (**best**): Electrons "**avoid**" one another (**Fermi hole**) and are in **different spatial regions** (orbitals) and so **repel one another the least**

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C $2p_x^2$ or $2p_x2p_y$?

$2p_x^2$ are in **same orbital** and so must have **greater** electron-electron **repulsion**

What about electrons in different 2p orbitals?

$2p_x2p_y$ can have **spins parallel** and so **decreased** repulsion (Fermi hole).

Both configurations have the **same nuclear attraction** (Z_{eff} and no inner loops).

Hence $2p_x2p_y$ (or $2p_x2p_z$ or $2p_y2p_z$) **more stable**.



8

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N $2p_x^22p_y$ or $2p_x2p_y2p_z$?

9

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N $2p_x^22p_y$ or $2p_x2p_y2p_z$?

In $2p_x^22p_y$ the $2p_x$ is in **same orbital** and so must have **greater** electron-electron **repulsion**

In $2p_x2p_y2p_z$ all spins are parallel and so there are **only Fermi holes** and so **reduced repulsion**.

Hence $2p_x2p_y2p_z$ is **more stable**.



10

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O $2p_x2p_y^22p_z$ or $2p_x2p_y2p_z3s$?

11

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O $2p_x 2p_y^2 2p_z$ or $2p_x 2p_y 2p_z 3s$?

$2p_x 2p_y^2 2p_z$ has **increased electron repulsion** (Fermi clump).

$2p_x 2p_y 2p_z 3s$ has **decreased electron repulsion** (Fermi hole).

$2p_x 2p_y^2 2p_z$ has **greater nuclear attraction** since the $n = 2$ orbitals are more bound than $n = 3$ orbitals.

Nuclear attraction more important than electron repulsion, and so $2p_x 2p_y^2 2p_z$ is more stable.



12

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F $2p_x^2 2p_y^2 2p_z$ or $2p_x 2p_y^2 2p_z 3s$?



13

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F $2p_x^2 2p_y^2 2p_z$ or $2p_x 2p_y^2 2p_z 3s$?

$2p_x^2 2p_y^2 2p_z$ has **increased electron repulsion** (Fermi clump).

$2p_x 2p_y^2 2p_z 3s$ has **decreased electron repulsion** (Fermi hole).

$2p_x^2 2p_y^2 2p_z$ has **greater nuclear attraction** since the $n = 2$ orbitals are more bound than $n = 3$ orbitals.

Nuclear attraction more important than electron repulsion, and so $2p_x^2 2p_y^2 2p_z$ is more stable.



14

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Ne $2p_x^2 2p_y^2 2p_z^2$ or $2p_x^2 2p_y^2 2p_z 3s$?



15

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Ne $2p_x^2 2p_y^2 2p_z^2$ or $2p_x^2 2p_y^2 2p_z^2 3s$?

$2p_x^2 2p_y^2 2p_z^2$ has larger Z_{eff} , since 2p electrons do not shield

$2p_x^2 2p_y^2 2p_z^2 3s$ has less electron repulsion but much smaller Z_{eff} , since $n = 3$ electron shield nearly completely.



16

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Na $2p_x^2 2p_y^2 2p_z^2 3s$ or $2p_x^2 2p_y^2 2p_z^2 3p$?



17

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Na $2p_x^2 2p_y^2 2p_z^2 3s$ or $2p_x^2 2p_y^2 2p_z^2 3p$?

3s **inner loop** means 3s has **more attraction** than 3p.

Hence $2p_x^2 2p_y^2 2p_z^2 3s$ **more stable** (analogous to $1s^2 2s$ being more stable than $1s^2 2p$).

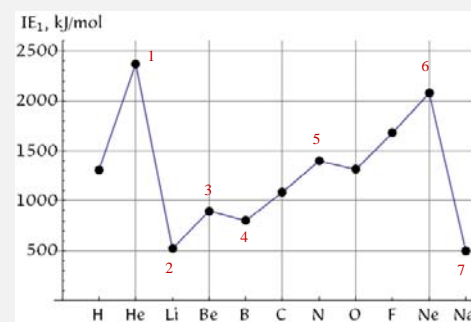


18

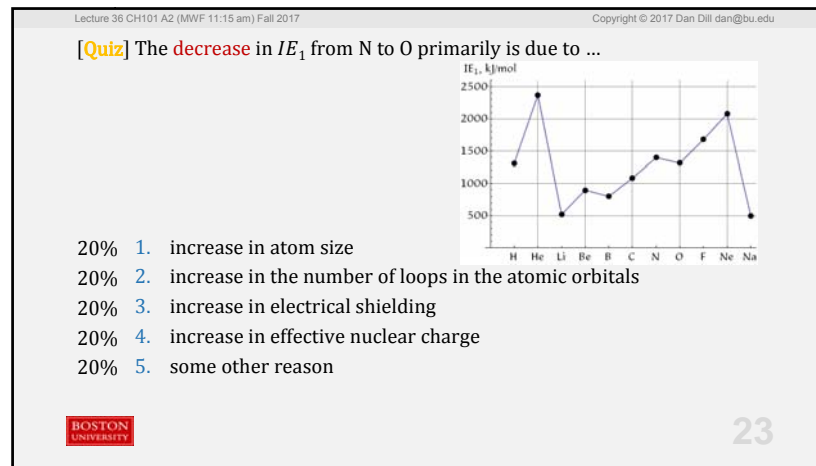
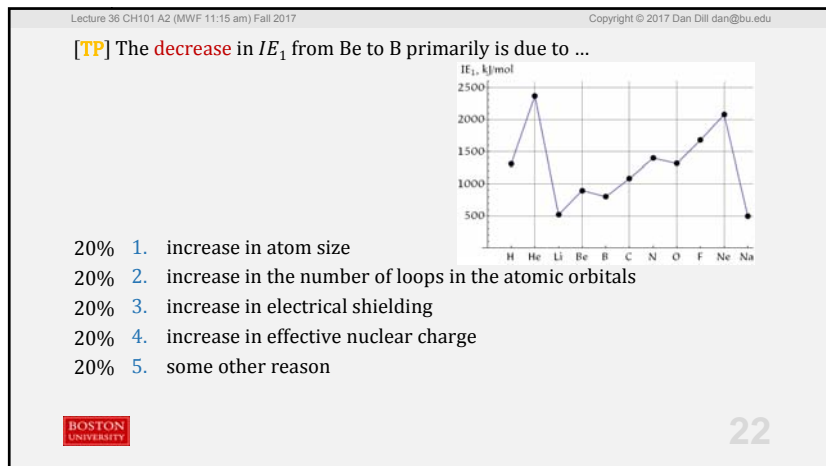
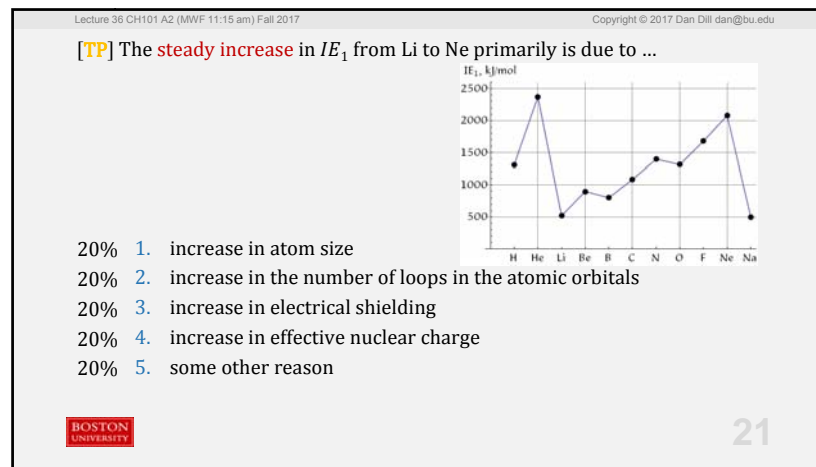
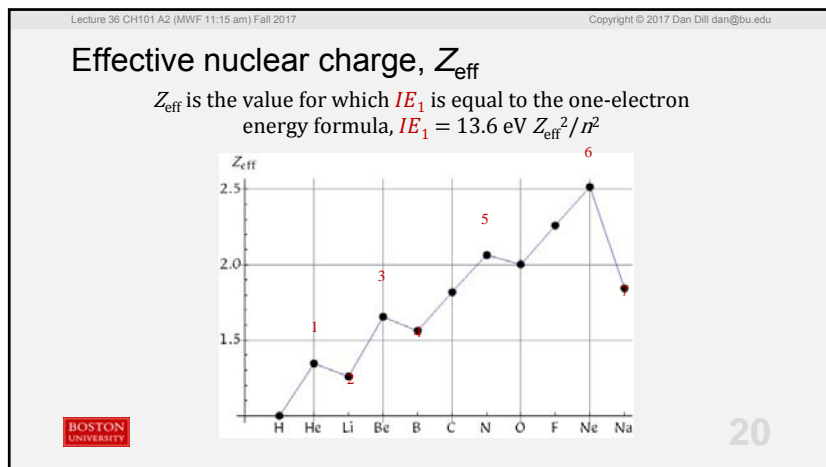
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First ionization energy, IE_1



19



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Bonding in diatomic molecules
<http://goo.gl/1h0S9C>

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Atoms interact by mixing **waves**

AO "+" AO \rightarrow 2 MO's
 "+" means **mixing** (not addition!)

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1s molecular orbitals:
<http://quantum.bu.edu/CDF/101/1sMolecularOrbitals.cdf>

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Relative AO phase determines MO character

here the different phases of the p-orbital are labelled positive and negative – this can be confusing and so is best avoided

here the different phases of the p-orbital are shown by shading one half and not the other

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σ MO's have cylindrical symmetry

Antibonding orbitals are designated with a * e.g. σ^* , or π^*

we can rotate about this axis without changing the MOs

both MOs have rotational symmetry about the axis through the two nuclei

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1σ and $1\sigma^*$

combine out-of-phase

combine in-phase

nodal plane

the two 1s orbitals combining out-of-phase to give an antibonding orbital

the two 1s orbitals combining in-phase to give a bonding orbital

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1σ and $1\sigma^*$

Energy

Nodal plane

σ^* -molecular orbital (antibonding)

σ -molecular orbital (bonding)

Mahaffy et al., Figure 10.20, p. 400

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43

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σ is “bonding” and σ^* is “antibonding”

Antibonding orbitals are designated with a * e.g. σ^* , or π^*

we can rotate about this axis without changing the MOs

both MOs have rotational symmetry about the axis through the two nuclei

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44

