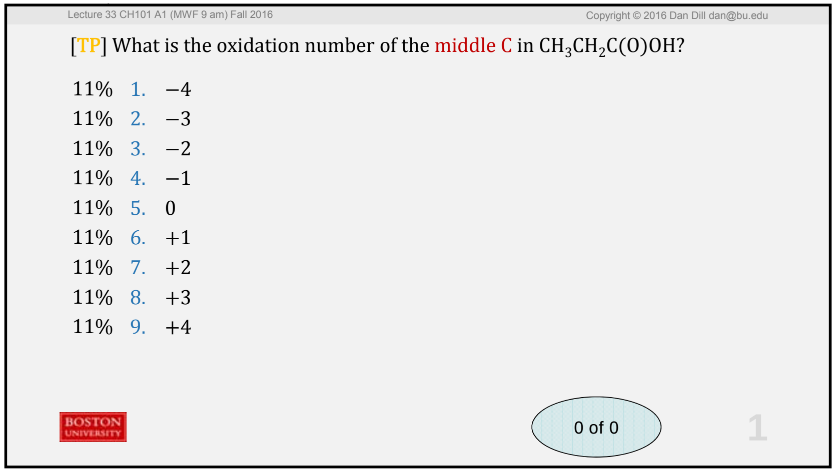
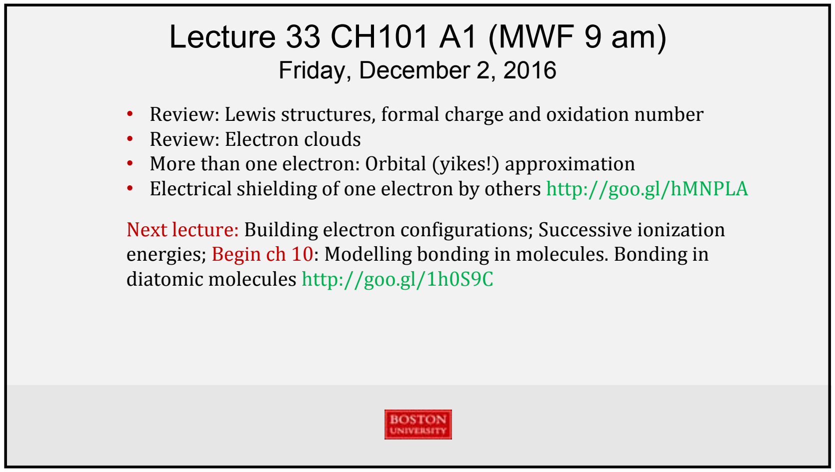


[TP] What is the oxidation number of the middle C in $CH_3CH_2C(O)OH$?

11%	1.	−4
11%	2.	−3
11%	3.	−2
11%	4.	−1
11%	5.	0
11%	6.	+1
11%	7.	+2
11%	8.	+3
11%	9.	+4

0 of 0

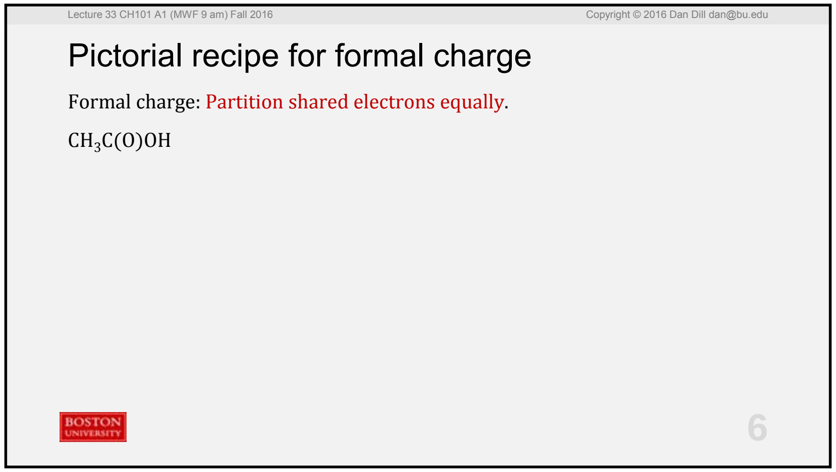


Lecture 33 CH101 A1 (MWF 9 am)

Friday, December 2, 2016

- Review: Lewis structures, formal charge and oxidation number
- Review: Electron clouds
- More than one electron: Orbital (yikes!) approximation
- Electrical shielding of one electron by others http://goo.gl/hMNPLA

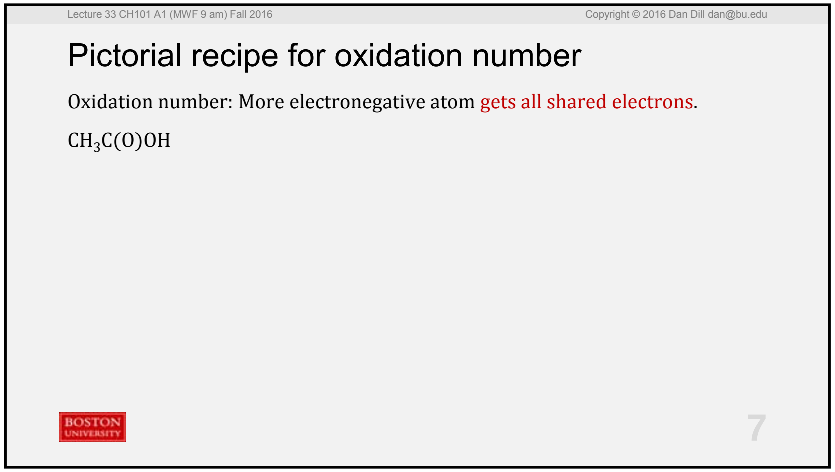
Next lecture: Building electron configurations; Successive ionization energies; Begin ch 10: Modelling bonding in molecules. Bonding in diatomic molecules http://goo.gl/1h0S9C



Pictorial recipe for formal charge

Formal charge: Partition shared electrons equally.

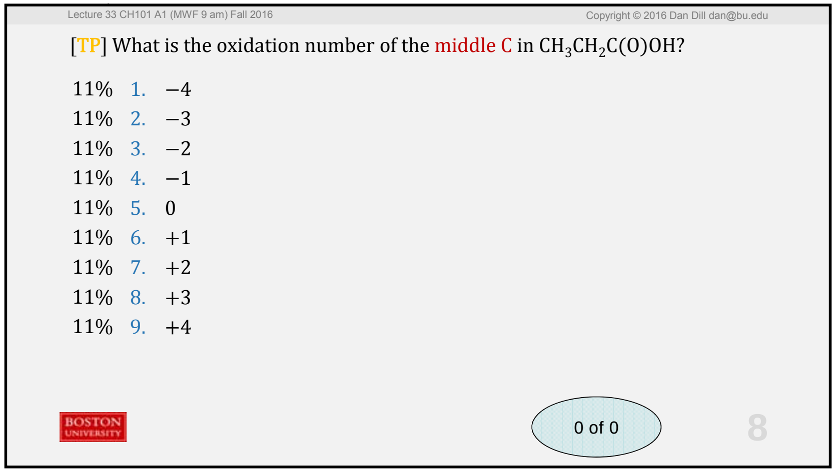
$CH_3C(O)OH$



Pictorial recipe for oxidation number

Oxidation number: More electronegative atom gets all shared electrons.

$CH_3C(O)OH$



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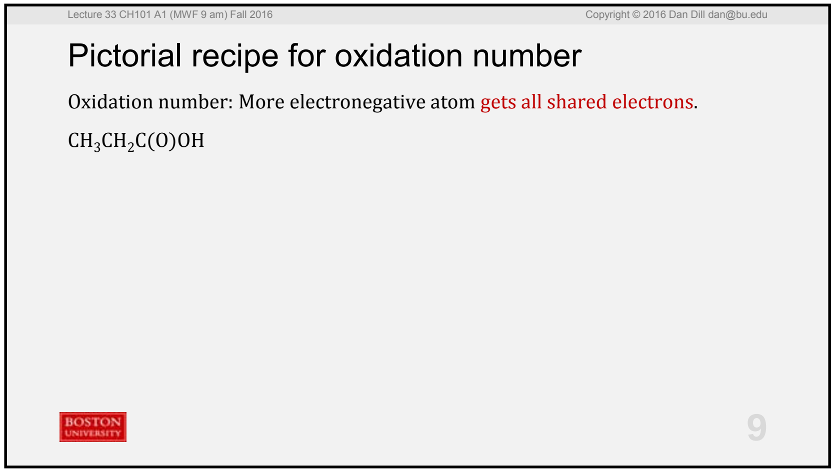
[TP] What is the oxidation number of the middle C in $CH_3CH_2C(O)OH$?

11% 1. −4
11% 2. −3
11% 3. −2
11% 4. −1
11% 5. 0
11% 6. +1
11% 7. +2
11% 8. +3
11% 9. +4

0 of 0

8



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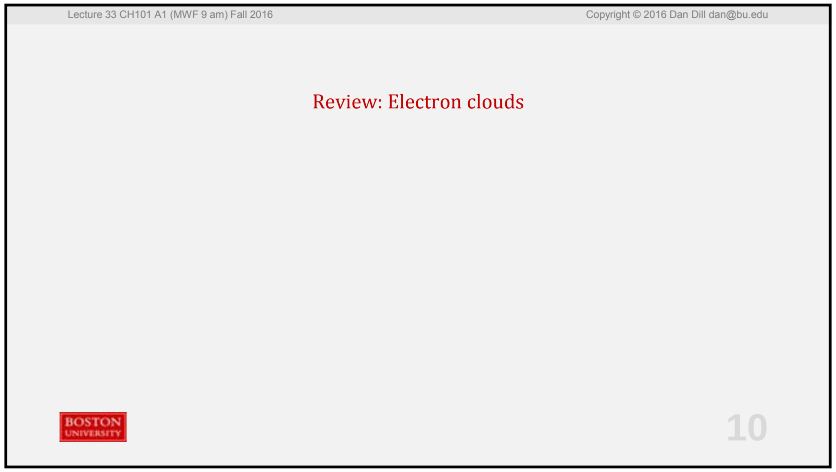
Pictorial recipe for oxidation number

Oxidation number: More electronegative atom gets all shared electrons.

$CH_3CH_2C(O)OH$

9



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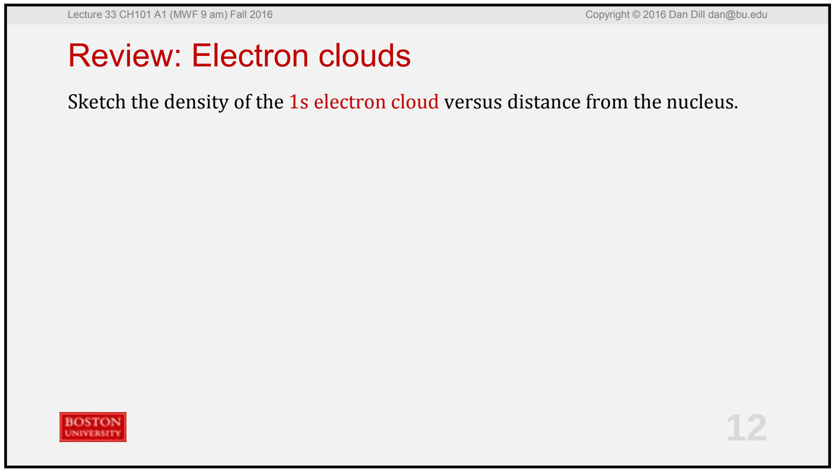
Review: Electron clouds

10



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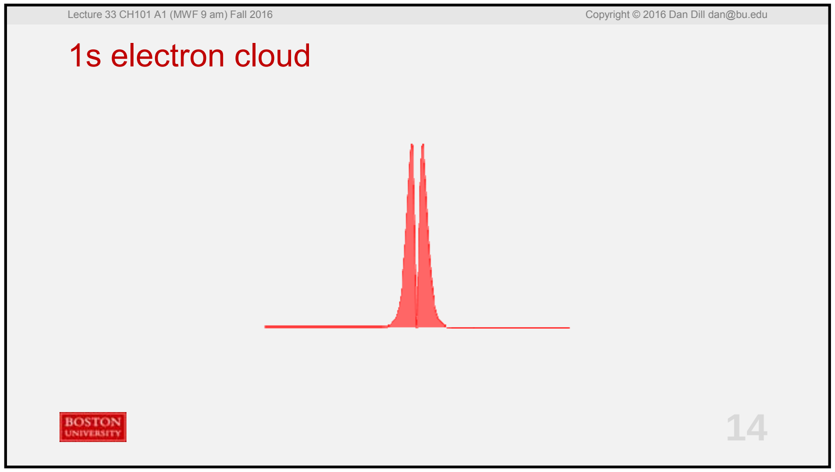
Review: Electron clouds

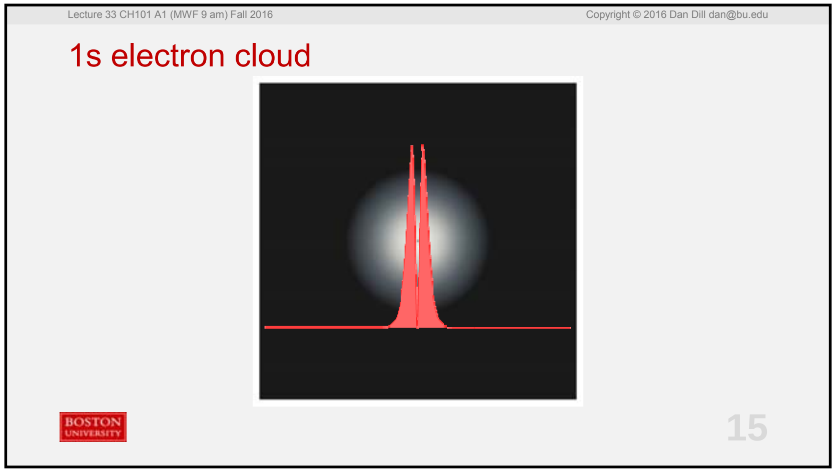
Sketch the density of the 1s electron cloud versus distance from the nucleus.

12

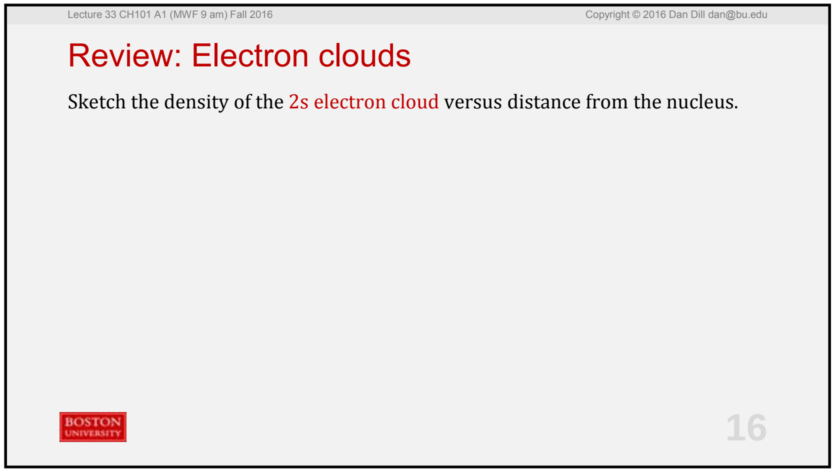
1s electron cloud



1s electron cloud



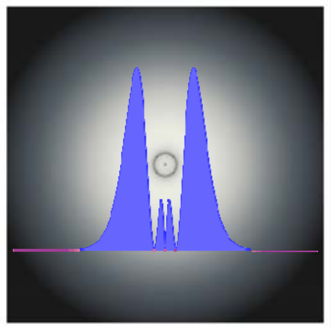
1s electron cloud



Review: Electron clouds

Sketch the density of the 2s electron cloud versus distance from the nucleus.

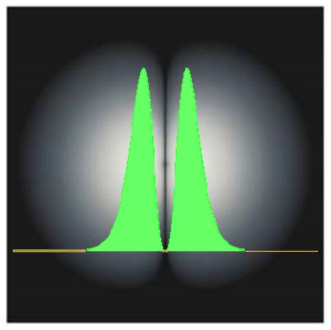
2s electron cloud



Review: Electron clouds

Sketch the density of the 2p electron cloud versus distance from the nucleus.

2p electron cloud

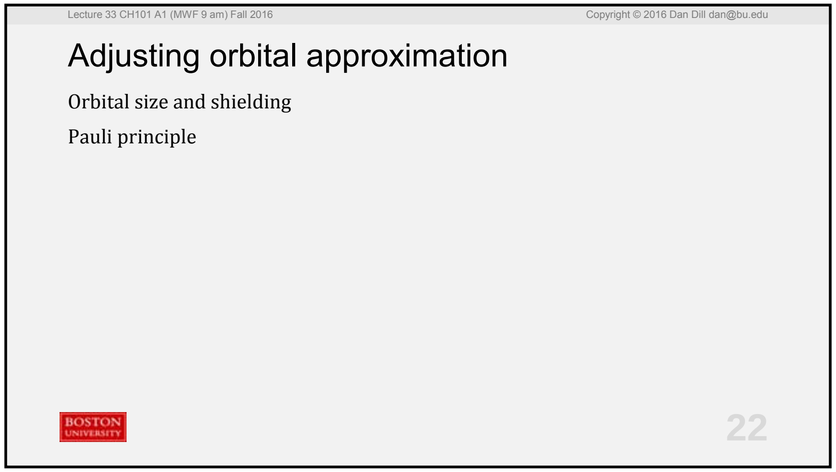


Orbital (!) approximation

Assign electrons to one-electron waves; for historical reasons these are called orbitals (yikes!).

This assignment would be exact if electrons did not repel one another.

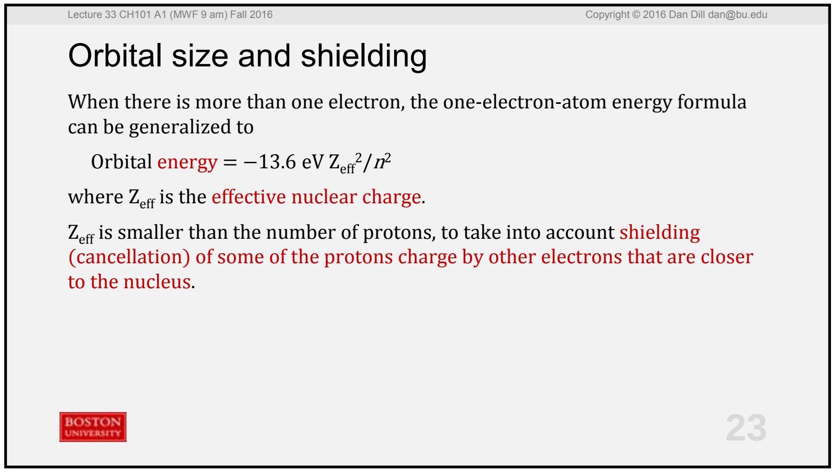
Because electron clouds are diffuse, repulsion is relatively small and so the orbital approximation is a good starting point.



Adjusting orbital approximation

Orbital size and shielding

Pauli principle



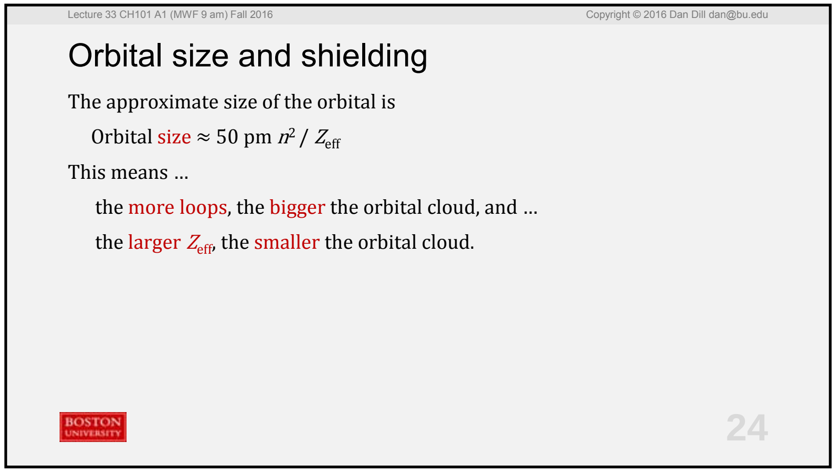
Orbital size and shielding

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

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

where Z_{eff} is the effective nuclear charge.

Z_{eff} is smaller than the number of protons, to take into account shielding (cancellation) of some of the protons charge by other electrons that are closer to the nucleus.



Orbital size and shielding

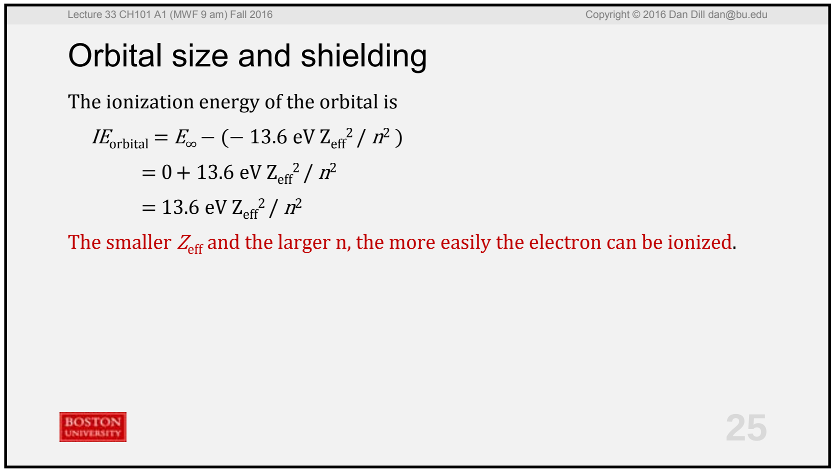
The approximate size of the orbital is

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

This means …

the more loops, the bigger the orbital cloud, and …

the larger Z_{eff}, the smaller the orbital cloud.



Orbital size and shielding

The ionization energy of the orbital is

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

The smaller Z_{eff} and the larger n, the more easily the electron can be ionized.

Demonstration:
Electrical shielding

Electrical shielding of one electron by others

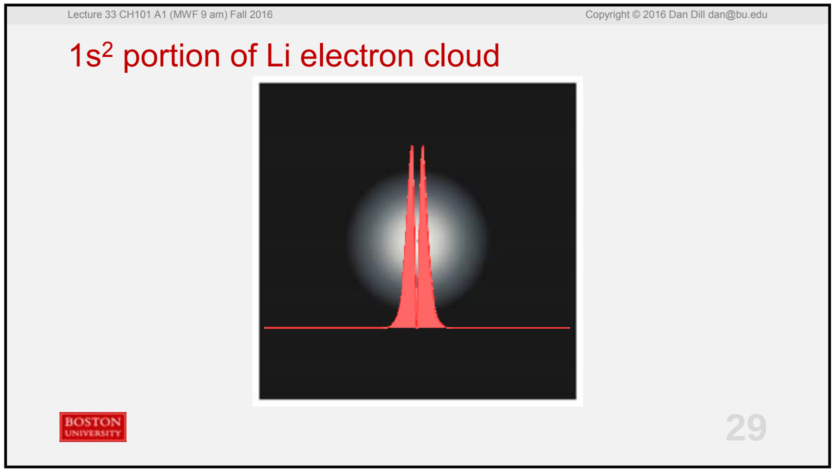
http://goo.gl/hMNPLA

The goal: Why $1s^2 2s$ and not $1s^2 2p$

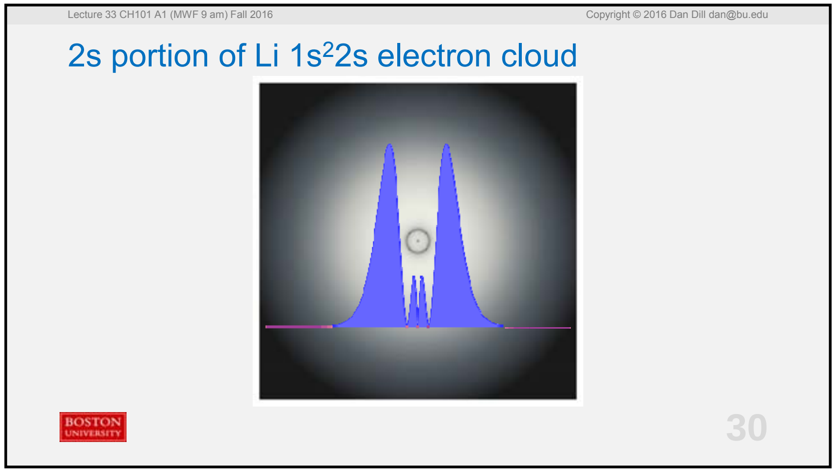
The Li atom electron configuration $1s^2 2s$ is more stable than $1s^2 2p$.

The reason is, the 2s electron feels a greater nuclear charge, Z_{eff}, than does the 2p electron.

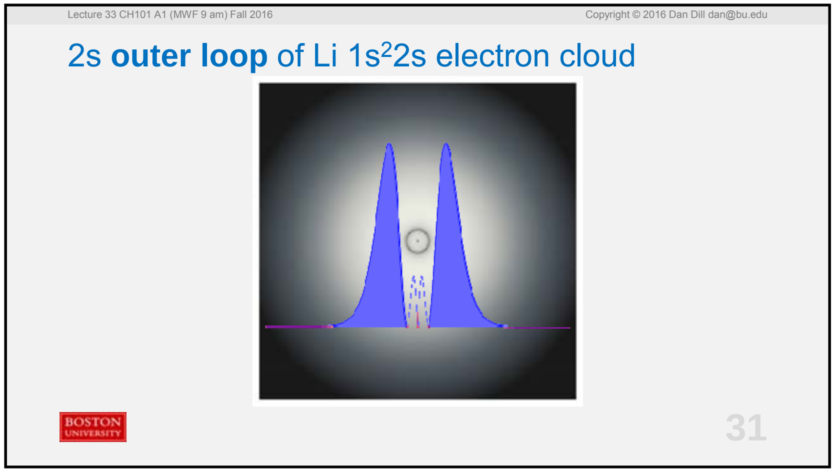
The following illustrations (http://goo.gl/hMNPLA) show qualitatively why this is so.



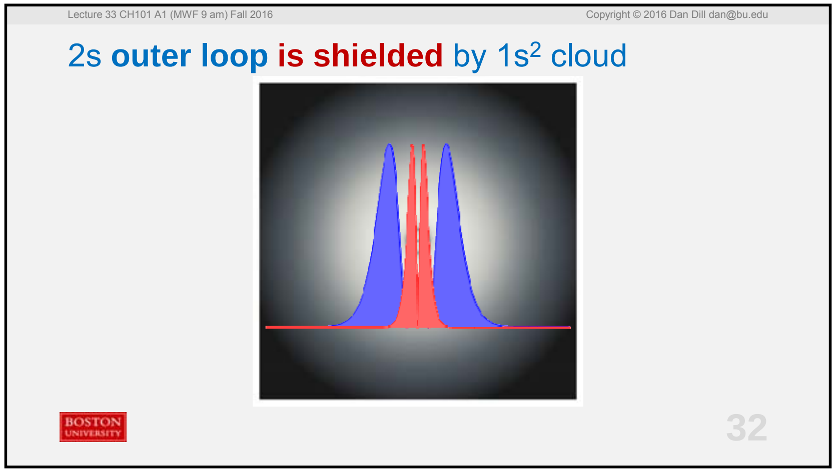
$1s^2$ portion of Li electron cloud



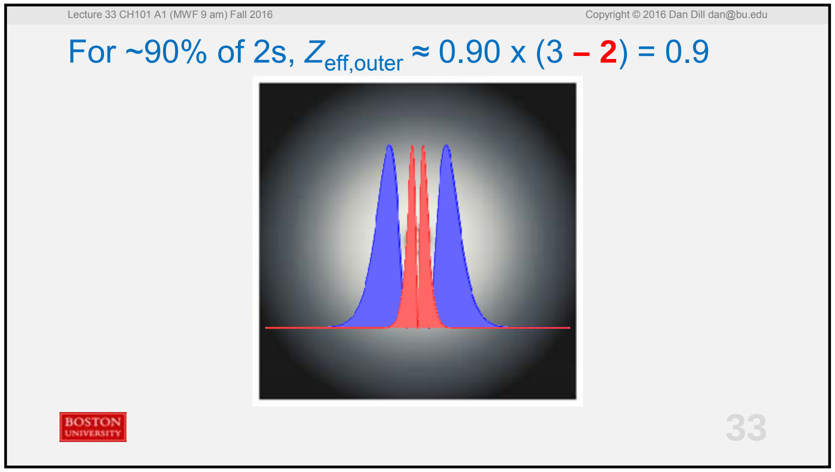
2s portion of Li $1s^22s$ electron cloud



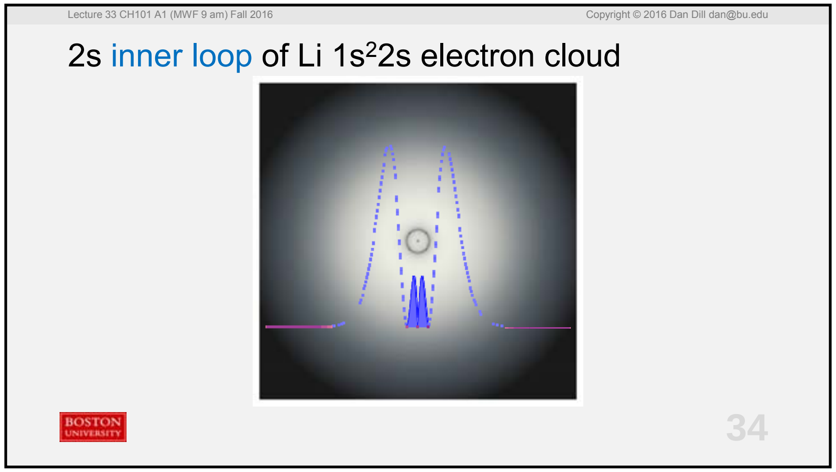
2s **outer loop** of Li $1s^22s$ electron cloud



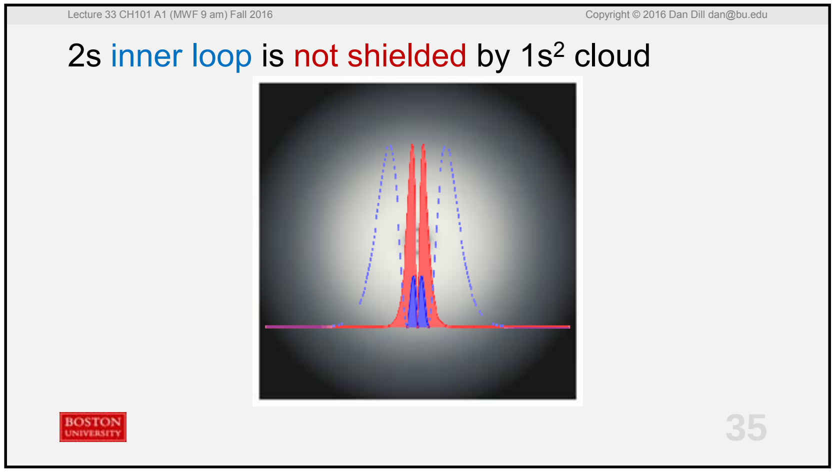
2s **outer loop is shielded** by $1s^2$ cloud



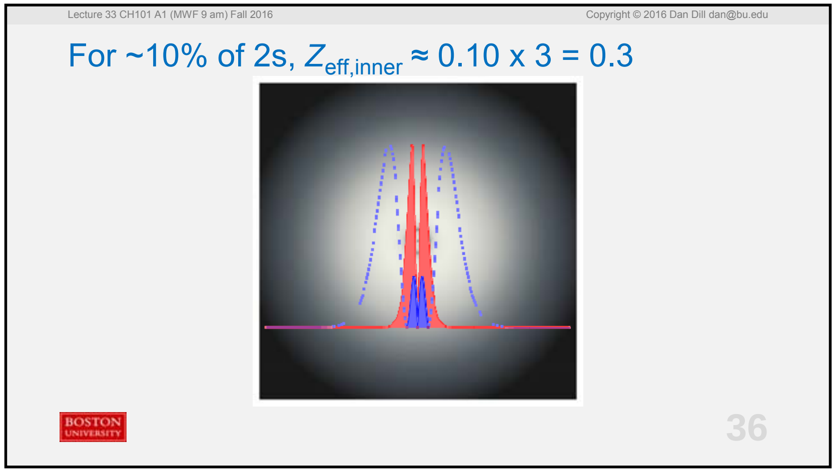
For ~90% of 2s, $Z_{\text{eff,outer}} \approx 0.90 \times (3 - \mathbf{2}) = 0.9$



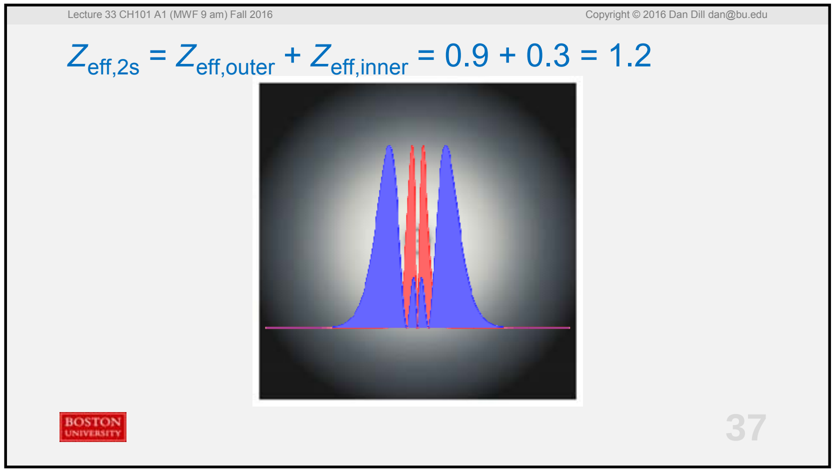
2s inner loop of Li $1s^22s$ electron cloud



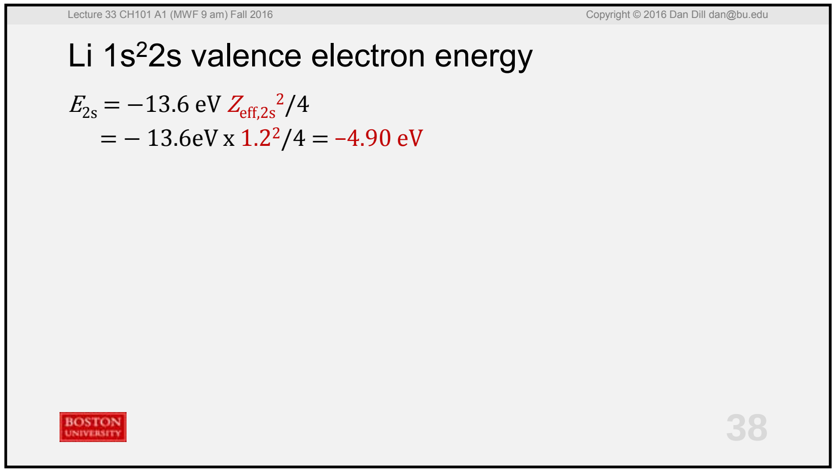
2s inner loop is not shielded by $1s^2$ cloud



For ~10% of 2s, $Z_{\text{eff,inner}} \approx 0.10 \text{ x } 3 = 0.3$

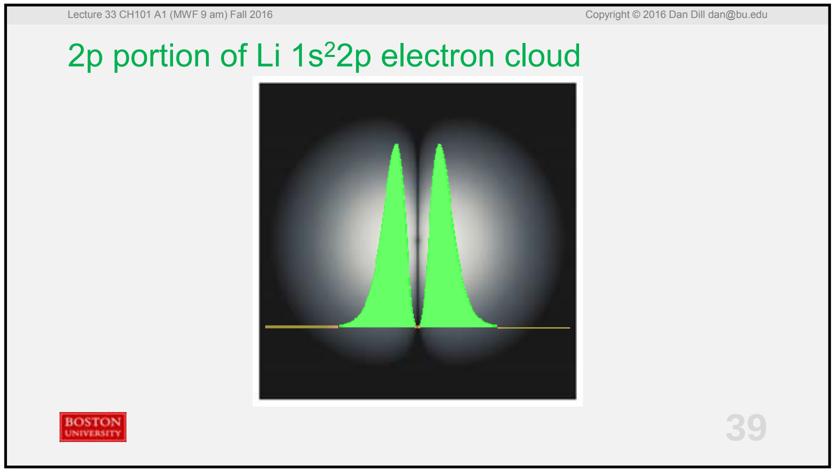


$Z_{\text{eff,2s}} = Z_{\text{eff,outer}} + Z_{\text{eff,inner}} = 0.9 + 0.3 = 1.2$

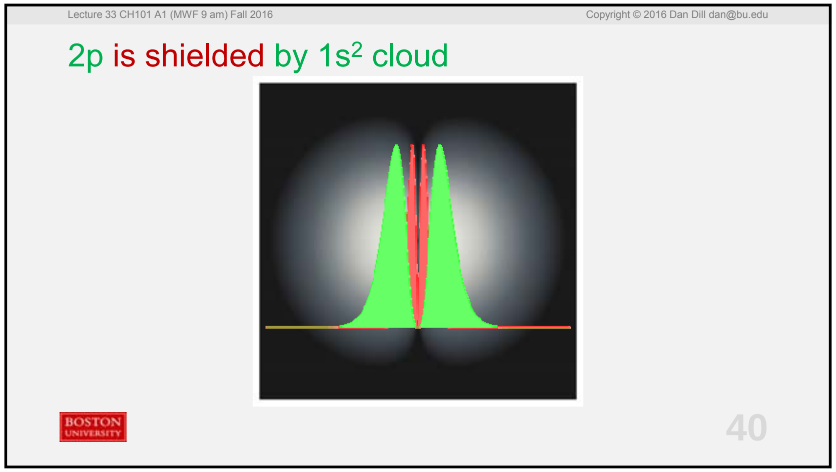


Li $1s^2 2s$ valence electron energy

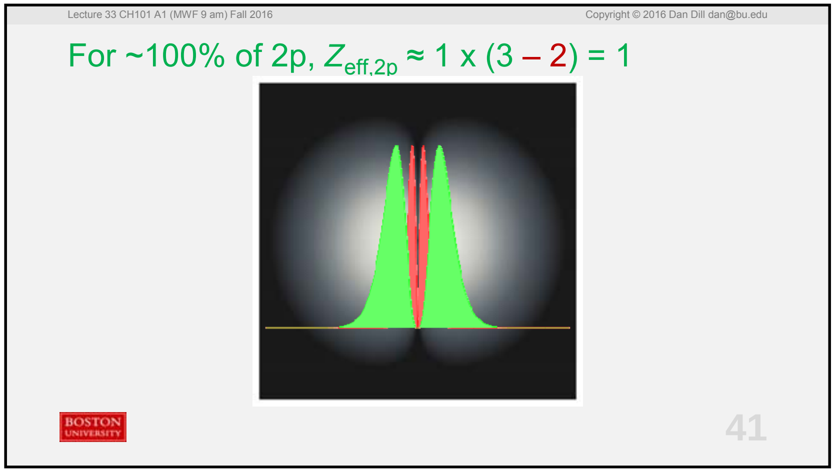
$$E_{2s} = -13.6\text{ eV } Z_{\text{eff},2s}{}^2/4$$
$$= -13.6\text{eV x } 1.2^2/4 = -4.90\text{ eV}$$



2p portion of Li $1s^2 2p$ electron cloud



2p is shielded by $1s^2$ cloud



For ~100% of 2p, $Z_{\text{eff},2p} \approx 1 \text{ x } (3 - 2) = 1$

Li 1s²2p valence electron energy

$E_{2p} = -13.6\text{ eV } Z_{\text{eff,2p}}{}^2/4$

$= -13.6\text{ eV x } 1^2/4 = -3.40\text{ eV}$

Li 1s²2s more stable than Li 1s²2p

$E_{2s} = -13.6\text{ eV } Z_{\text{eff,2s}}{}^2/4$

$= -13.6\text{eV x } 1.2^2/4 = -4.90\text{ eV}$

$E_{2p} = -13.6\text{ eV } Z_{\text{eff,2p}}{}^2/4$

$= -13.6\text{ eV x } 1^2/4 = -3.40\text{ eV}$

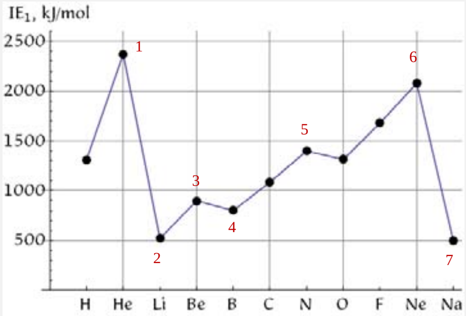
The reason is, the 2s electron feels a greater nuclear charge, Z_{eff}, than does the 2p electron.

Building electron configurations

Make a sketch of IE versus atom, for H through Na.

The goal: Understand the pattern of stability across the periodic table.

$IE_1 = 13.6\text{ eV } Z_{\text{eff}}{}^2/n^2$



Li $1s^3$?

Not possible, since at least two electrons would have the same spin in the same orbital.

Such an electron wave vanishes everywhere and so there can be no atom with this configuration.

Energy order of relative spins (Pauli)

Key point: “spin” = magnetic moment, either up or down

↑↑ never; ↑↓ (worst) > ↑ ... ↓ > ↑ ... ↑ (best)

Li $1s^22s$ or $1s^22p$?

The 2s inner loop escapes the shielding of the $1s^2$ part of the electron cloud.

The 2p has no inner loop and so would be more shielded by the $1s^2$ part of the electron cloud.

Hence, the 2s electron experiences slightly greater nuclear charge (Z_{eff}) and so it is more tightly held than the 2p electron would be.

So, $1s^22s$ is more stable than $1s^22p$

Be $2s^2$ or $2s2p$?

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

But, the 2s inner loops result in greater nuclear attraction than the 2p.

Nuclear attraction trumps electron repulsion, and so $2s^2$ is more stable.

B $2s^3$ or $2s^22p_x$ or $2s^22p_y$ or $2s^22p_z$?

$2s^3$ is not possible for the same reason as $1s^3$ is not.

Either $2s^22p_x$ or $2s^22p_y$ or $2s^22p_z$ are possible and equivalent.

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?

Energy order of relative spins (Pauli)

Key point: “spin” = magnetic moment, either up or down

↑↑ never; ↑↓ (worst) > ↑ ... ↓ > ↑ ... ↑ (best)

↑↓ (worst): Electrons in same spatial region (orbital) and so repel one another the most

↑ ... ↓: Electrons clump together (Fermi clump) in different spatial regions (orbitals) and so repel somewhat less

↑ ... ↑ (best): Electrons “avoid” one another (Fermi hole) and are in different spatial regions (orbitals) and so repel one another the least

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.

N $2p_x^2 2p_y$ or $2p_x 2p_y 2p_z$?

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

In $2p_x 2p_y 2p_z$ all spins are parallel and so there are only Fermi holes and so reduced repulsion.

Hence $2p_x 2p_y 2p_z$ is more stable.

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

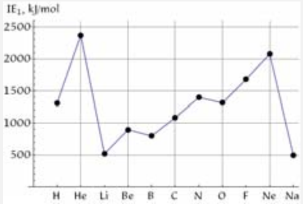
$2p_x 2p_y^2 2p_z$ has increased electron repulsion (Fermi clump).

$2p_x 2p_y 2p_z 3s$ 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 trumps electron repulsion, and so $2p_x 2p_y^2 2p_z$ is more stable.

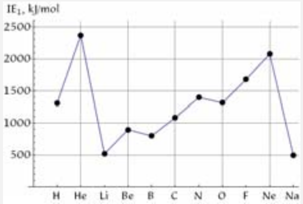
[TP] The decrease in IE_1 from Be to B primarily is due to ...



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

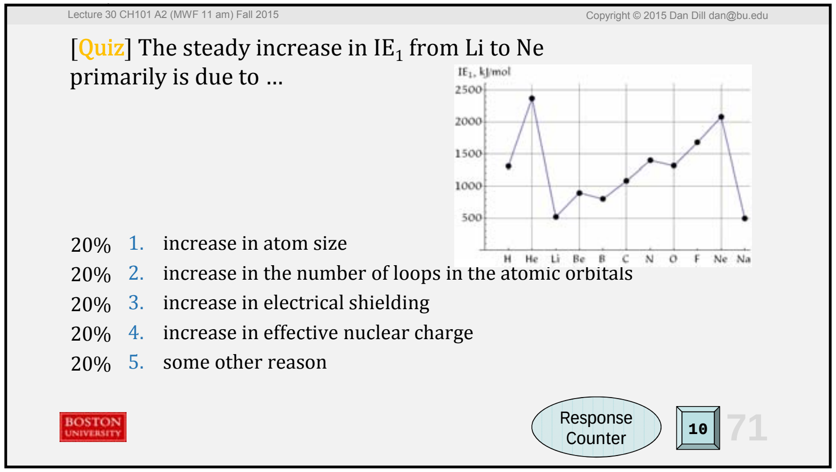
Response Counter 10

[TP] The decrease in IE_1 from N to O primarily is due to ...



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

Response Counter 10



[Quiz] The steady increase in IE$_1$ from Li to Ne primarily is due to …

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

Successive ionization energies

Sketch the first five ionization energies of calcium.

Successive ionization energies

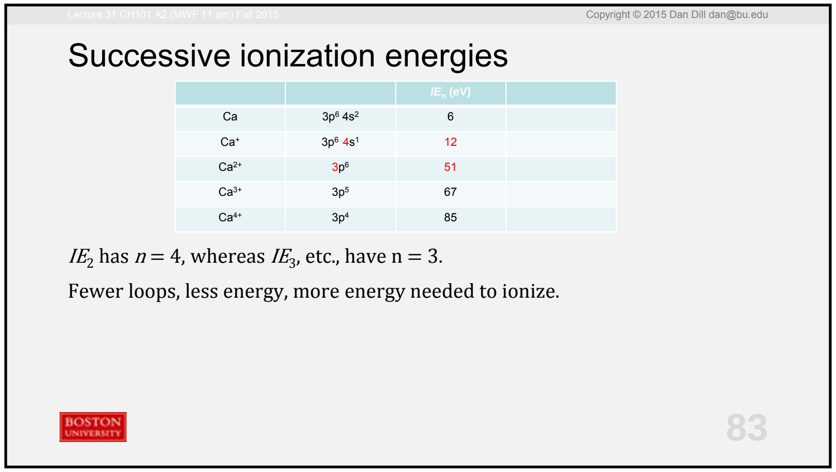
		IE_n (eV)	
Ca	$3p^6\ 4s^2$	6	
Ca^+	$3p^6\ 4s^1$	12	
Ca^{2+}	$3p^6$	51	
Ca^{3+}	$3p^5$	67	
Ca^{4+}	$3p^4$	85	

Successive ionization energies

		IE_n (eV)	
Ca	$3p^6\ 4s^2$	6	
Ca^+	$3p^6\ 4s^1$	12	
Ca^{2+}	$3p^6$	51	
Ca^{3+}	$3p^5$	67	
Ca^{4+}	$3p^4$	85	

The largest change from one to the next is $IE_3 - IE_2 = 39$ eV.

Why is this change so large compare to the other successive changes?



Successive ionization energies

		IE_n (eV)	
Ca	$3p^6\ 4s^2$	6	
Ca^+	$3p^6\ 4s^1$	12	
Ca^{2+}	$3p^6$	51	
Ca^{3+}	$3p^5$	67	
Ca^{4+}	$3p^4$	85	

IE_2 has $n = 4$, whereas IE_3, etc., have n = 3.

Fewer loops, less energy, more energy needed to ionize.

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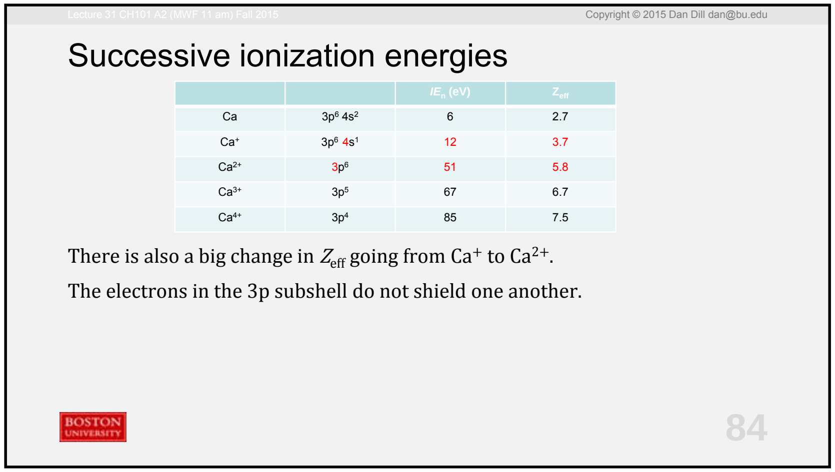

Successive ionization energies

		IE_n (eV)	Z_{eff}
Ca	$3p^6\ 4s^2$	6	2.7
Ca^+	$3p^6\ 4s^1$	12	3.7
Ca^{2+}	$3p^6$	51	5.8
Ca^{3+}	$3p^5$	67	6.7
Ca^{4+}	$3p^4$	85	7.5

There is also a big change in Z_{eff} going from Ca^+ to Ca^{2+}.

The electrons in the 3p subshell do not shield one another.

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