Chemistry 1B-02 Session 5-6
Fall 2016

Chemistry 1B
Fall 2016

sessions 5-6
Chapter 12
pp. 557-569
*(569-571)

1

What can you do to become famous?

[and win a cool $1.2 million]?]

2

STUDY QUANTUM MECHANICS

When scientists wanted to simulate complex chemical processes on computers, they used to have to choose between software that was based on classical Newtownian physics or ones based on quantum physics. But the academy said the three laureates developed computer models that "opened a gate between these two worlds."

3

Molecular Mechanics at UCSC

Prof Ilan Benjamin
Prof. Yuan Ping

4

2012 Nobel in QUANTUM physics

5

aims for lectures 5-6: many electron atoms

- electron spin, "the 4th quantum number and the Pauli exclusion principle
- effective nuclear charge, Z_{eff} the "net" attraction for an electron in a many-electron atom
- knowledge of the principal quantum number (n) and Z_{eff} for and atom's valence electrons leads to an understanding of:
  - $E_{2s} < E_{2p}$
  - $E_{3p} < E_{3d}$
  - E_{3d} vs E_{4s}
- Hund's Rule and electron configuration in many-electron atoms the Aufbau Principle

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new considerations for many-electron atoms
(somewhat different 'order' of presentation than Zumdahl

- **how does increased atomic number (Z) and the presence of other electrons affect orbital energies?**
- **how does one "fill up" the available orbitals in many-electron atoms**

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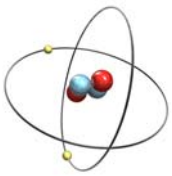
multi-electron atoms

Electron Spin

Electronic Configurations

8

did the Schrodinger equation "work" for helium ??



$\mathcal{H}_{helium}\Psi = E_{helium}\Psi$???

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many-electron atoms and Schrödinger Equation (pp 557-558)

Although the Schrödinger equation, $\mathcal{H}\Psi=E\Psi$, for polyelectronic atoms (and molecules) cannot be solved exactly (mathematically)

Numerical computer calculations give solutions that **agree perfectly with experiment** ✓

Year	Method	Quantal/Experimental $-E$	
1924	experimental, Lyman (1924)	2.9035	exp
1998	exp., Bergeson *et al.* (1998)	2.903 693 775	
1929	var., 38 param., Hylleraas (1929)	2.9037	calc
1993	relativ. Drake (1993)	2.903 700 023	

but solutions are very complex .

$$\Psi(s,u,t) = Ne^{-(1/2)u}\sum_{l,m,n} C_{l,m,n} s^l t^m u^n e^{-s} t^m \quad (2)$$

so- We can (and will!!) use the hydrogen-like orbitals as a very good approximation to the exact solutions of the Schrödinger equation for many-electron atoms.

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aims for sessions 5-6: many electron atoms

this video

- electron spin, "the 4th quantum number and the Pauli exclusion principle
- effective nuclear charge, Z_{eff} the "net" attraction for an electron in a many-electron atom

in next class

- knowledge of the principal quantum number (n) and Z_{eff} for and atom's valence electrons leads to an understanding of:
  - $E_{2s} < E_{2p}$
  - $E_{3p} < E_{3d}$
  - E_{3d} vs E_{4s}
- Hund's Rule and electron configuration in many-electron atoms the Aufbau Principle

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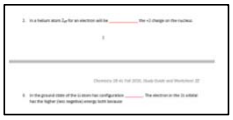
worksheet III sections I.1-2 and II.1-3



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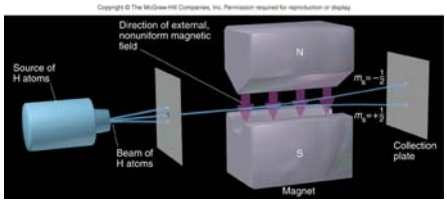
Stern-Gerlach Experiment

- Stern-Gerlach experiment (fig. 8-1 Silberberg)



https://quantum-reality.net/2015/11/03/the-stern-gerlach-experiment/

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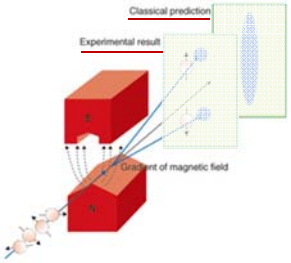
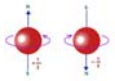
the 4th quantum number: spin



https://www.ntt-review.jp/archive/ntttechnical.php?contents=ntr201209fa4_s.html

the electron has two possible spin states with spin quantum numbers
m_s=+½ or m_s=–½

spin up and spin down



http://www.quantum-field-theory.net/discovery-electron-spin/

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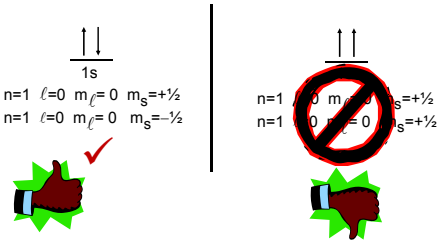
Pauli exclusion principle (PEP) (sec 12.10)

no two electrons can have the same four quantum numbers:



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many-electron atoms

He, Li, Be, B, C, N, O, F, Ne ……

- greater nuclear charge (Z) than hydrogen (Z=1)
- more electrons than hydrogen (one-electron)

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where we are heading !!! chapter 12

- Quantum mechanics describes many-electron atoms by filling hydrogen-like orbitals with the atom's electrons in a manner consistent with the Pauli Exclusion Principle.
- This description allows us to understand the **energies** of electrons in atoms and ions, the **relative sizes** of atoms and ions, and the **chemical reactivity** and other properties of various elements.

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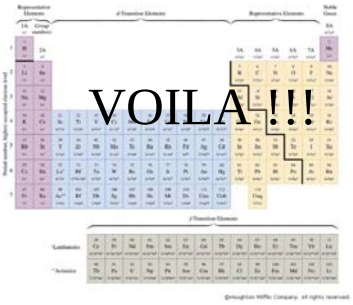
voila



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electronic configuration

electronic configuration: specification of which orbitals the electrons occupy in an atom (or molecule) [*and possibly the spins of electrons*]

e.g. for H: 1s or $\underset{1s}{\uparrow}$

He: $1s^2$ or $\underset{1s}{\uparrow\downarrow}$

C: $1s^2 2s^2 2p^2$ $\underset{2p}{\uparrow\ \uparrow\ \ }$

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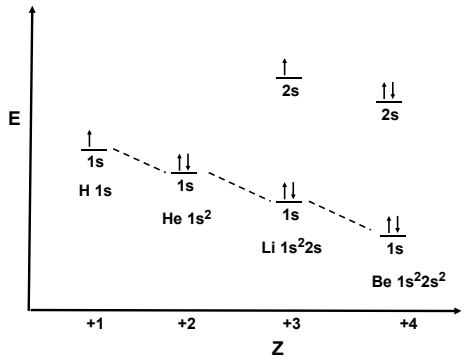
configurations (for 1s and 2s levels) ground states (preview)



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remembering from H atom

- Dependence of energy and average radius of electron in a hydrogen orbital on:
  n and Z

$$E_n = -\frac{m_e e^4}{8h^2\varepsilon_0^2}\frac{Z^2}{n^2} = -(2.18\times10^{-18}\ J)\frac{Z^2}{n^2}$$

$$\bar{r} \approx (5.29\times10^{-11} m)\frac{n^2}{Z}$$

- Holds **EXACTLY** for 1-electon atoms and ions: H, He^+, Li^{2+},Be^{3+}, ...
  Here Z is "regular" nuclear charge with Z=1, 2, 3, 4,

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ionization energy (section problem (HW2 #11, S3)

- ionization energy **(IE)** : the energy required to remove an electron from an atom, ion, or molecule in the gas phase
- X (g) + IE ⟶ X^+(g) +e^- (absorbs energy IE: *endothermic,* **+** *sign for IE*)
- $\mathbf{IE_n}$ for state n is energy difference between state **n** and state **n→∞**

$$(I.E.)_n = (E_\infty - E_n) = -E_n = +(2.18\times10^{-18}\ J)\frac{Z^2}{n^2}$$

- similar to the work function Φ in the photoelectric effect, except IE refers to gas phase ionization where Φ refers to removal of electron from the solid

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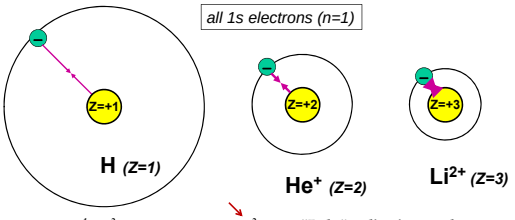
Energy of H 1s vs He^+ 1s vs Li^{2+} 1s (still 1 electron)



$$E_n = -\frac{m_e e^4}{8h^2\varepsilon_0^2}\frac{Z^2}{n^2} = -(2.18\times10^{-18}\ J)\frac{Z^2}{n^2}$$

"Bohr" radius in gas phase

$$\bar{r}_{avg} \approx (0.529\times10^{-10}\text{m})\ \frac{n^2}{Z}$$

increase Z
- more attraction
- lower *(more negative)* energy (*ie higher IE*)
- smaller r_{avg}

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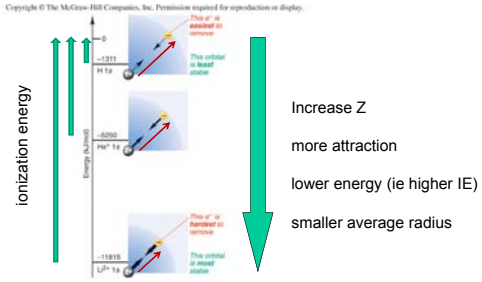
Silberberg Figure 8.3
Energy of H 1s vs He^+ 1s vs Li^{2+} 1s (still 1 electron)



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what happens when other electrons are present: effective nuclear charge (p 559)

Important Factoids in Understanding Effective Nuclear Charge

- **Energy dependence on n and Z_{eff}**

$$E_n \approx -(2.18\times10^{-18}\ J)\frac{Z_{eff}^2}{n^2}$$

- **Z_{eff} and shielding *(attraction-repulsion)***

$$Z_{eff} = Z^{+} - (\text{effect of electron repulsions})^{-}$$

$$Z_{eff} = Z - (\text{shielding of other electrons})$$

1s electron 'feels' full Z=+2 nuclear attraction

- **electrons in same shell:**

He^+ 1s vs He $1s^2$

the two 1s electrons shield one another from the Z=+2 nuclear pull

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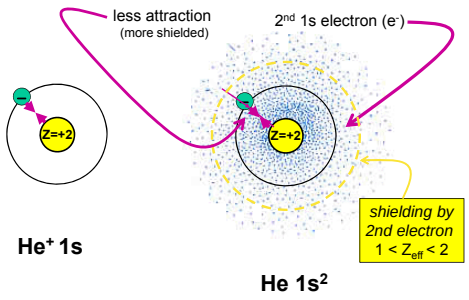
He^+ vs He (what positive charge does a 1s electron 'see' ?)



He^+ 1s

He $1s^2$

more shielding → lower Z_{eff} → larger average radius

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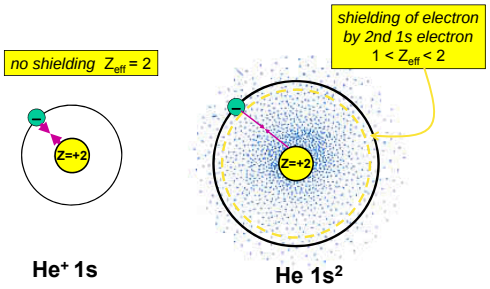
*He^+ vs He (what **net** positive charge does a 1s electron 'see' ?)*



He^+ 1s

He $1s^2$

lower Z_{eff} → larger average radius
lower Z_{eff} → lower attractive forces

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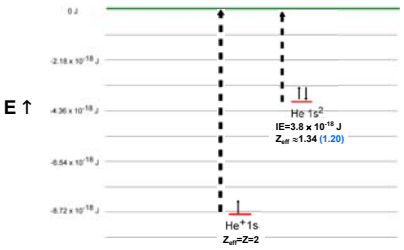
Energy of He $1s^2$ vs He^+ 1s (HO fig 12.2)

Z_{eff} and Ionization Energies

Z_{eff} (He^+ 1s) > Z_{eff} (He $1s^2$)



$$IE \approx (2.18\times10^{-18}\ J)\frac{Z_{eff}^2}{n^2} \qquad Z_{eff} \approx \left[\frac{n^2\ IE}{2.18\times10^{-18}\ J}\right]^{1/2}$$

this is approximate way to calculate Z_{eff}; other techniques give slightly different numbers

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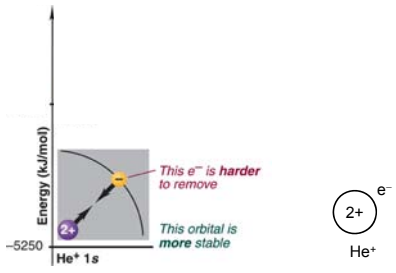
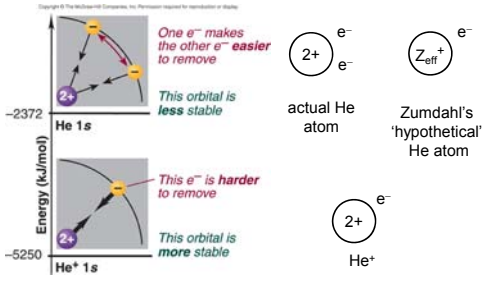
energy of He $1s^2$ vs He^+ 1s (same shell shielding) Zumdahl (p. 558-9)



29

Silberberg figure 8.4A: energy of He $1s^2$ vs He^+ 1s (same shell shielding) Zumdahl (p. 556-8) [558-559]7th



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Z_{eff}: effective nuclear charge

what about shielding if the electrons are in different shells

Li^{2+} 2s vs Li $[1s^2]$ 2s

shielding the 2s electron

would you expect electrons in an inner shell to provide less or greater shielding effects than electrons in the same shell ?

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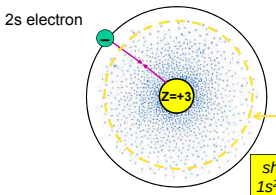
Z_{eff} for 2s electron in Li $1s^2 2s$



$IE_{experimental} = 0.86 \times 10^{-18} J$

$(Z_{eff})_{2s} \approx \left[\frac{n^2\ IE_{2s}}{2.18 \times 10^{-18} J}\right]^{1/2} = 1.26$

Li $1s^2 2s$

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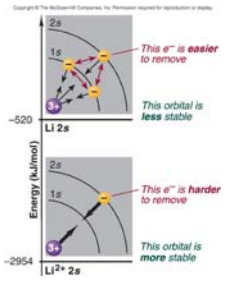
figure 8.4 B (Silb) shielding by inner shell electrons



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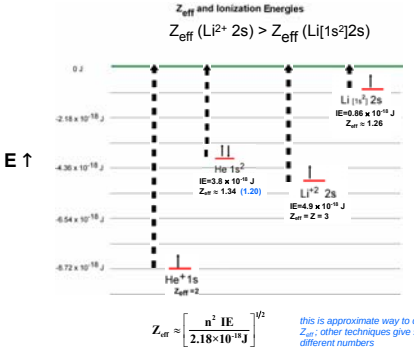
*Energy of Li^{2+} **2s** vs Li $[1s^2]$ **2s** (HO Fig. 12.3)*



$Z_{eff} \approx \left[\frac{n^2\ IE}{2.18 \times 10^{-18} J}\right]^{1/2}$

this is approximate way to calculate Z_{eff}; other techniques give slightly different numbers

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same shell shielding He $1s^2$ vs inner shell shielding $Li1s^2 2S$

how would one expect the shielding of 1s electron for another 1s electron [same shell] to compare to the shielding of a 1s electron for a 2s electron [different shells] ?

shielding of same shell **?** shielding of outer shell by inner shell

He $1s^2$ vs $Li1s^2 2s$

How so ? *[Z_{eff}=$Z_{nucleus}$-shielding of other electrons]*

He : $Z_{eff}(1s) \approx 1.34 = +2 -$ shielding of other 1s electron

shielding of other 1s electron = **0.66**

Li : $Z_{eff}(2s) \approx 1.26 = +3 -$ shielding of two 1s electrons

shielding of each inner shell 1s electron $= \frac{1.74}{2} =$ **0.87**

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DONE FOR NOW !!

http://www.tunnel.ru/i/post/350182/3501828039/2063662981/at948236225.gif

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take home material from: Video03

- Stern-Gerlach electron spin +½ and –½
- Pauli Exclusion Principle (PEP)
- effective nuclear charge: Z_{eff}
  - $+Z_{nuclear\ chage}$ — repulsion (shielding) by other electrons
  - shielding greater from electron in inner shell than electron in same shell [from electrons 'inside' or closer to nucleus]
  - $E_n \approx -\frac{m_e e^4}{8h^2\varepsilon_0^2}\frac{Z_{eff}^2}{n^2} = -(2.18\times10^{-18}\ J)\frac{Z_{eff}^2}{n^2} \qquad \bar{r} \approx (5.29\times10^{-11} m)\frac{n^2}{Z_{eff}}$

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in many-electron atoms
how do the energies of the 2s and 2p orbitals compare?

In 1-electron atoms (H-atom) and 1-electron ions (He^+, Li^{2+} …), a 2s and 2p orbital will have the .. **SAME** .. energy

fig. 12.23 for 1-electron atoms and ions

now Z_{eff}
and the effect of penetration of inner shell electron density by electrons in the same shell (e.g. 2s electron vs 2p electron)

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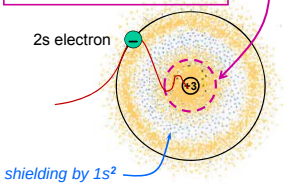
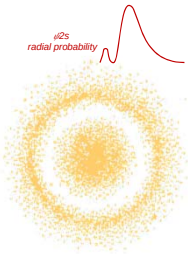
Z_{eff} for 2s vs 2p: 2p and 2s have SAME energy in 1-electon ion

'penetration' by 2s electron of $1s^2$ shielding GIVES INCREASED Zeff



Li $1s^2$2s
$Z_{eff} \approx 1.26$



actual 2s electron density (one radial node; one inner maximum in radial probability)

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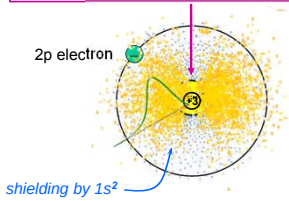
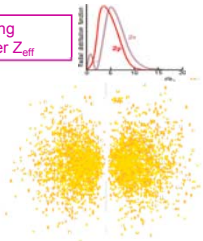
Z_{eff} for 2s vs 2p

no (less) 'penetration' of $1s^2$ shielding by 2p electron GIVES relatively smaller Z_{eff}



Li $1s^2$2p

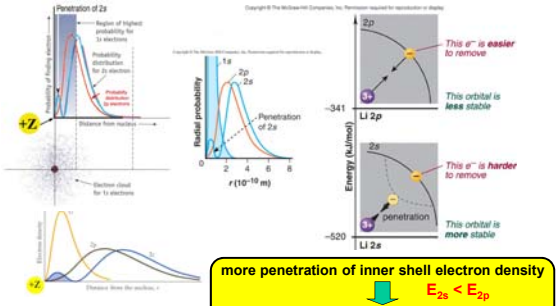
Z_{eff} for 2s > Z_{eff} for 2p
$E_{2s} < E_{2p}$



actual 2p electron density (no radial nodes; no 'inner maxima' in radial probability)

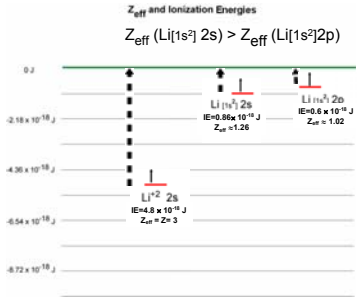
40

Z_{eff} for 2s vs 2p (handout fig. 12.4)



more penetration of inner shell electron density
$E_{2s} < E_{2p}$
electron see's more +Z and has greater Z_{eff}

*Energy of Li [$1s^2$] **2s** vs Li [$1s^2$] **2p** (HO Fig. 12.5): penetration*



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how do the energies of the 2s and 2p orbitals compare in many-electron atoms?

- **Configurations and valence-level orbital diagrams** ➡
- **Hund's rule** ➡
- **2nd row aufbau fig 8.8 (Sil)** ➡

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3s, 3p, 3d, 4s orbital energy ordering

- **Increasing Z_{eff} due to increasing penetration effects (figure HO 12Z.6);** ➡

  $(Z_{eff})_{3s} > (Z_{eff})_{3p} > (Z_{eff})_{3d}$

  $(E)_{3s} < (E)_{3p} < (E)_{3d}$
- **4s vs 3d (Z_{eff} vs n)** ➡
- **Orbital energy ordering fig 8.6 (Silb) (figure 8.13, Silb)** ➡

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configurations

- **Hund's rule**
  - **Energy ordering**
  - **Unambiguous [closed shell, 1e, (n-1)e's e.g. p^1, p^5, d^1,d^9]** ➡
  - **Ambiguous [e.g. p^2,p^3,p^4, $d^2 \rightarrow d^8$]** ➡
- **Examples (periodic table)** ➡
  - **ground state**
  - **excited state**
  - **not allowed configuration**
  - **transition metal cations**
  - **"exceptions"** ➡

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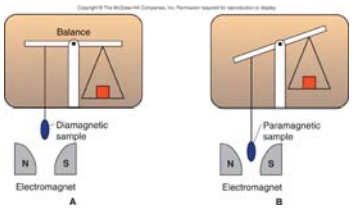
unpaired electrons and magnetic properties (Gouy balance)

Diamagnetic
• pushed out of magnet
• no unpaired electrons

Paramagnetic
• pulled into magnet
• unpaired electrons



Gouy Balance

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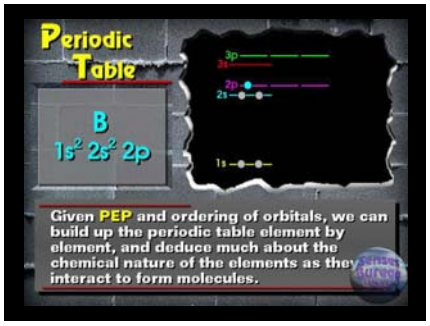
the Periodic Table



➡

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end of material sessions 5-6

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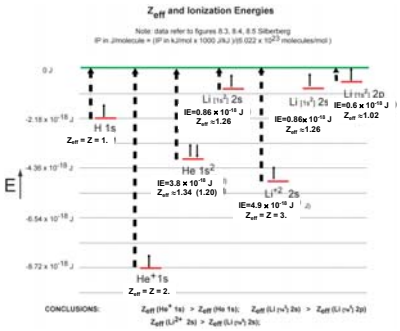
Z_{eff} and ionization potentials



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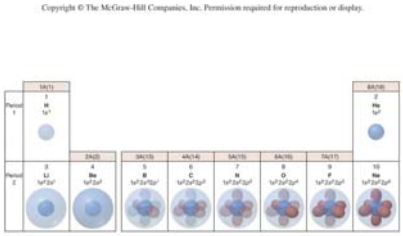
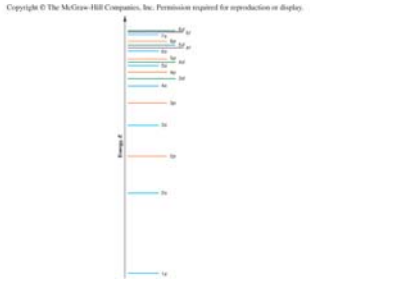
Silberberg figure 8.8



50

Silberberg figure 8.6



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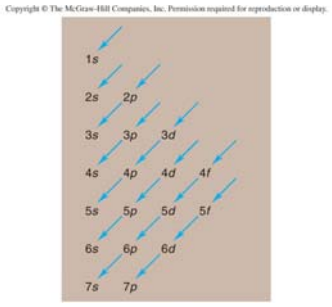
Silberberg figure 8.13



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Zumdahl figure 12.29

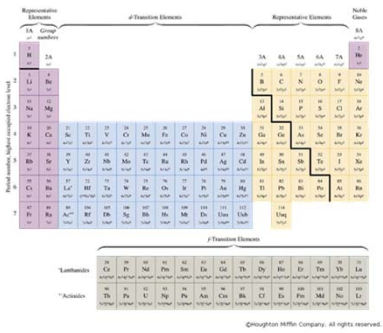

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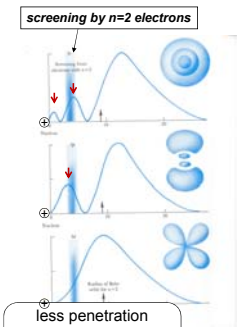
Figure HO 8.6: penetration of 3s vs 3p vs 3d; ***radial nodes = n-ℓ-1***



3s: 2 radial nodes
2 "inner electron density maxima"

3p: 1 radial node
1 "inner maxima"

3d: 0 radial nodes
0 "inner maxima"

less penetration
smaller Z_{eff}
higher energy

more penetration
larger Z_{eff}
lower Energy

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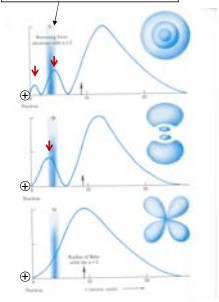
Figure HO 8.6: penetration of 3s vs 3p vs 3d; ***radial nodes = n-ℓ-1***

screening by n=2 electrons



3s: 2 radial nodes
2 "inner electron

3p: 1 radial node
1 "inner maxima"

3d: 0 radial nodes
0 "inner maxima"

more penetration
larger Z_{eff}
lower Energy

less penetration
smaller Z_{eff}
higher energy

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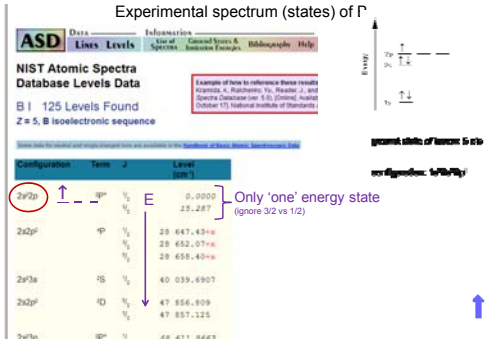
*Why B [He] $2s^2\ 2p^1$ is '**unambiguous**' ground state configuration*

Experimental spectrum (states) of B



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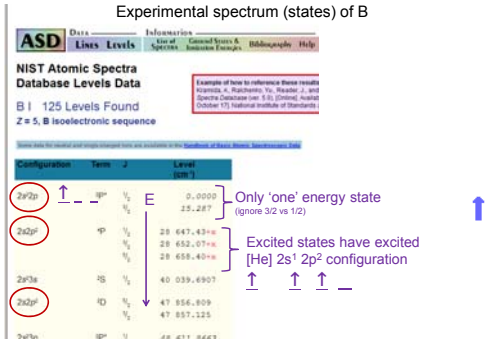
*Why B [He] $2s^2\ 2p^1$ is '**unambiguous**' ground state configuration*

Experimental spectrum (states) of B



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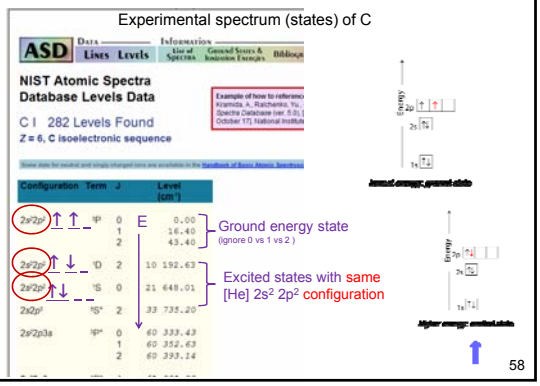
*Why C [He] $2s^2\ 2p^2$ is '**ambiguous**' ground state configuration*

Experimental spectrum (states) of C



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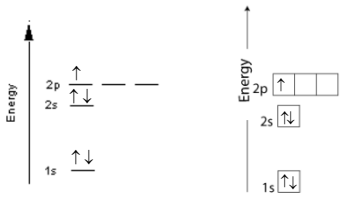
n=1 and n=2 energy diagram for multi-electron atoms



ground state of boron: 5 e's

configuration: $1s^2 2s^2 2p^1$ or [He] $2s^2 2p^1$

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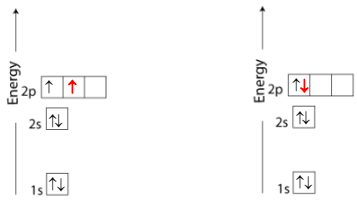
Hund's Rule

Friedrich Hund

for a given configuration, the lowest energy state will have the maximum number of electrons with parallel spins

carbon 6e's: $1s^2 2s^2 2p^2$ or [He] $2s^2 2p^2$



lowest energy: ground state

higher energy: excited state

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E_{3d} vs E_{4s} a contest between n and Z_{eff} !!!

$$E_n \approx -(2.18\times10^{-18}\ J)\frac{Z_{eff}^2}{n^2}$$

smaller n ⇒ lower (more negative) energy
larger Z_{eff} ⇒ lower (more negative) energy

who wins for lower energy?

3d vs 4s

n: 3 4 **3d wins for lower energy**

Z_{eff}: smaller (0 radial nodes) larger (3 radial nodes) **4s wins for lower energy**

and the energy winner is :

in neutral atoms Z_{eff} wins: $\mathbf{E_{4s} < E_{3d}}$
but in positive ions (e.g. Fe^{3+}) n wins: $\mathbf{E_{3d} < E_{4s}}$

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exceptions (p568)

The Aufbau Principle that we have been using is extremely useful in describing electronic configurations in atoms and ions. However since it is an 'approximation' to the actual (Schrödinger) wavefunctions, exceptions may be observed.

extra stability of half- or filled-shells:

^{23}V: $[^{18}Ar]\ 4s^2 3d^3$ ↑ ↑ ↑ _ _ *as expected*

^{24}Cr: $[^{18}Ar]\ 4s^2 3d^4$ ↑ ↑ ↑ ↑ _ *expected*

but **$[^{18}Ar]\ 4s^1$ ↑ $3d^5$ ↑ ↑ ↑ ↑ ↑** *observed (half-filled)*

^{28}Ni: $[^{18}Ar]\ 4s^2 3d^8$

~~^{29}Cu: $[^{18}Ar]\ 4s^2 3d^9$~~

but: ^{29}Cu: $[^{18}Ar]\ 4s^1 3d^{10}$ *filled* *half-filled*

In chemistry 1B-02 you will NOT be responsible for memorizing exceptions but just to 'explain' a given exception

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