

# ***Chemistry 1B***

## ***Fall 2016***

sessions 5-6

Chapter 12

pp. 557-569

\*(569-571)

What can you do to become famous?

*[and win a cool \$1.2 million]?*

# STUDY QUANTUM MECHANICS



The image is a promotional graphic for the Nobel Prize in Chemistry 2013. At the top left is a gold Nobel medal. The text "Nobelpriset 2013" is in the top left, and "The Nobel" is in the top right. The main title "The Nobel Prize in Chemistry 2013" is centered at the top. Below the title are three portraits of the laureates: Martin Karplus, Michael Levitt, and Arieh Warshel. Each portrait is accompanied by their name and affiliation. At the bottom, there is a Swedish quote: "För utvecklandet av flerskalemodeller för komplexa kemiska system."

Nobelpriset 2013

The Nobel

**The Nobel Prize in Chemistry 2013**



**Martin Karplus**  
Université de Strasbourg,  
France and Harvard  
University, Cambridge,  
MA, USA

**Michael Levitt**  
Stanford University School of  
Medicine, CA, USA

**Arieh Warshel**  
University of Southern  
California, Los Angeles, CA,  
USA

*"För utvecklandet av flerskalemodeller för komplexa kemiska system."*

When scientists wanted to simulate complex chemical processes on computers, they used to have to choose between software that was based on classical Newtonian

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."

# Molecular Mechanics at UCSC

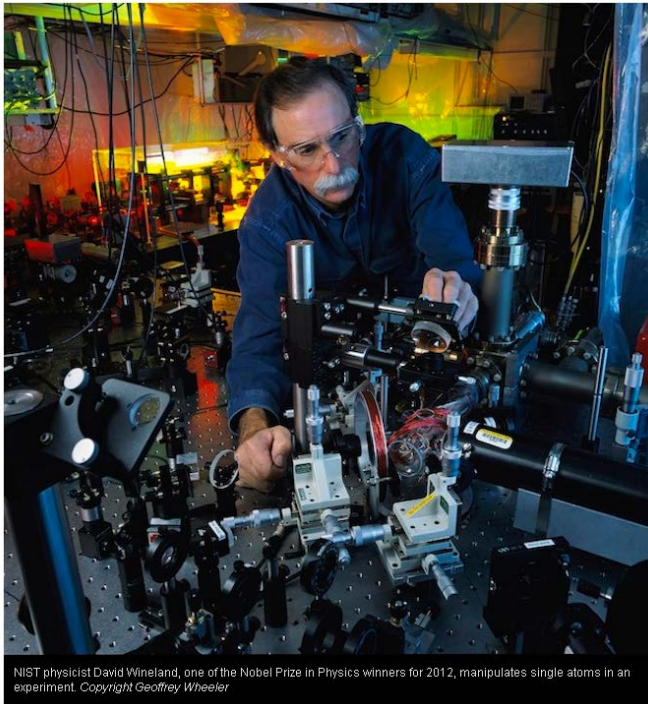


Prof Ilan Benjamin  
Prof. Yuan Ping

# 2012 Nobel in QUANTUM physics

## Nobel Awarded to Scientists Who Learned to Control Quantum Systems

By ScienceNow | October 9, 2012 | 2:41 pm | Categories: Physics



Nobelpriset 2012 The Nobel Prize 2012



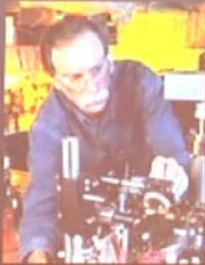

**LIVE** Mastering Particles in the Quantum World

KUNGL. VETENSKAPS AKADEMIEN  
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Ion(s) in a trap controlled by photons

Photon(s) in a cavity controlled by atoms

David Wineland Serge Haroche



Nobelprize.org

- electron spin, “the 4<sup>th</sup> quantum number and the Pauli exclusion principle
- effective nuclear charge,  $Z_{\text{eff}}$   
the “net” attraction for an electron in a many-electron atom
- knowledge of the principal quantum number ( $n$ ) and  $Z_{\text{eff}}$  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



- **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**

Chemistry IB -AL

multi-electron atoms

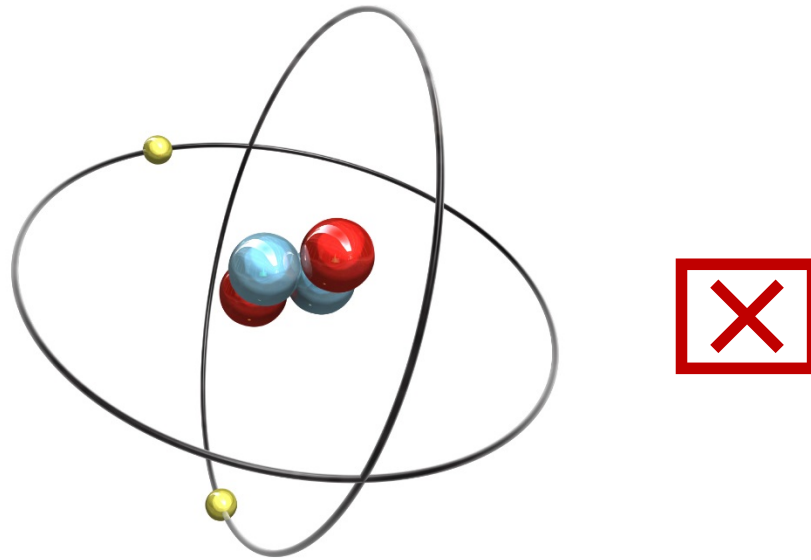
Electron Spin

Electronic Configurations



*did the Schrodinger equation “work” for helium ??*

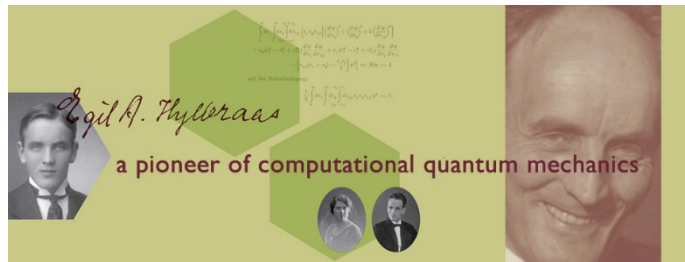
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$$\mathcal{H}_{\text{helium}} \Psi = E_{\text{helium}} \Psi \quad ???$$

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

but solutions are very complex .

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

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.

*this video*

- electron spin, “the 4<sup>th</sup> quantum number and the Pauli exclusion principle
- effective nuclear charge,  $Z_{\text{eff}}$   
the “net” attraction for an electron in a many-electron atom

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*in next class*

- knowledge of the principal quantum number ( $n$ ) and  $Z_{\text{eff}}$  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

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

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet III

## Learning Objectives and Worksheet III

### Chemistry 1B-AL Fall 2016

#### Lectures (5-6) Many Electron Atoms and the Aufbau Principle

Read pp. 557-569 (you will not be responsible for the material on pp-569-571; however the CHEM1B-AL staff would be more than happy to discuss these concepts with you)

#### Atomic orbital APPROXIMATION

To describe the electronic structure of atoms we will be using a model that is an approximation to the actual (exact) solutions to the Schrödinger equation. In this model the many-electron wavefunction is 'built' up by placing electrons into 'hydrogen-like' atomic orbitals.

#### I. Pauli Exclusion Principle (PEP)

1. What did the Stern-Gerlach experiment indicate?

2. What is Pauli Exclusion Principle as related to allowed orbital occupancy?

Addition information on Stern-Gerlach and electron 'spin' (University of Toronto):

<http://www.upscale.utoronto.ca/GeneralInterest/Harrison/SternGerlach/SternGerlach.html>

#### II. Energies of orbitals In many-electron atoms

1. In the hydrogen atom, and for all 1-electron ions, the energy of an electron in an orbital with quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$ ,  $m_s$  is given by  $E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{Z^2}{n^2} = -(2.18 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2}$ . For the energy of an electron in a many electron atom the nuclear charge  $Z$  is replaced by \_\_\_\_\_ which takes into account both  $Z$ , the \_\_\_\_\_ of the nucleus, and the repulsion ( $\sigma$ =shielding of nuclear charge) of the \_\_\_\_\_.
2. In a helium atom  $Z_{\text{eff}}$  for an electron will be \_\_\_\_\_ the +2 charge on the nucleus.

1

2. In a helium atom  $Z_{\text{eff}}$  for an electron will be \_\_\_\_\_ the +2 charge on the nucleus.

1

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet III

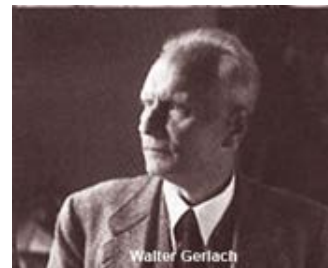
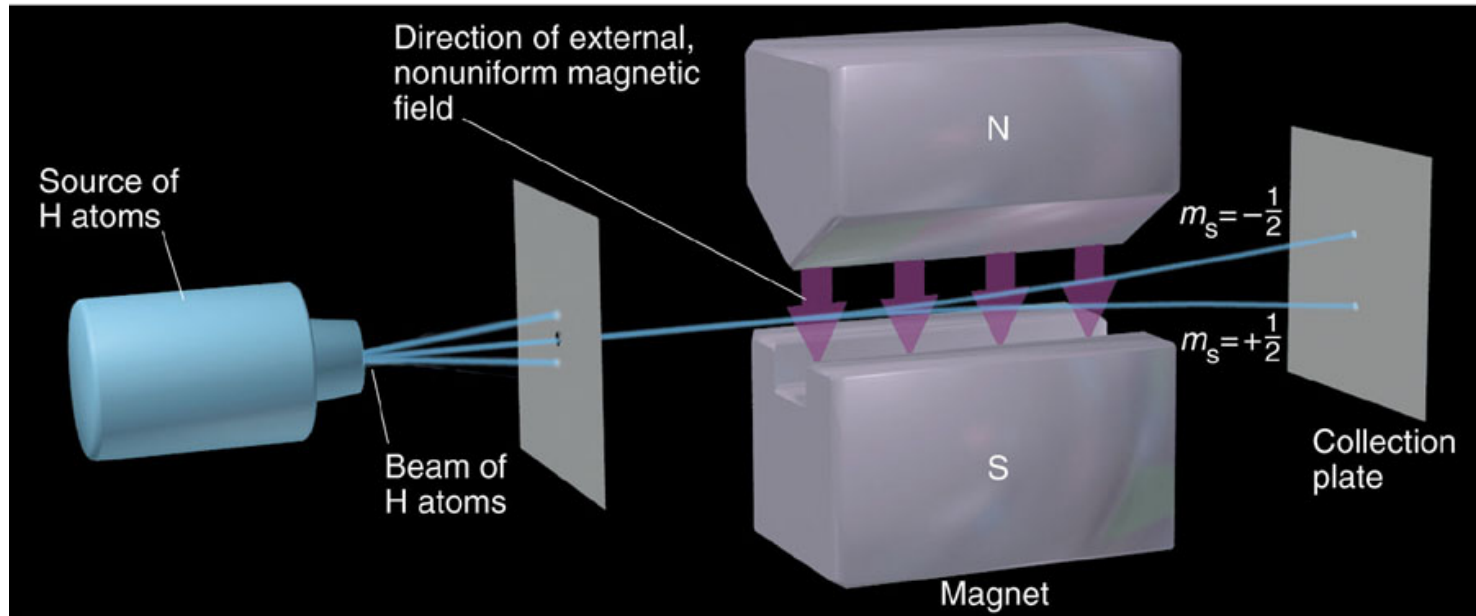
3. In the ground state of the Li atom has configuration \_\_\_\_\_. The electron in the 2s orbital has the higher (less negative) energy both because



# Stern-Gerlach Experiment

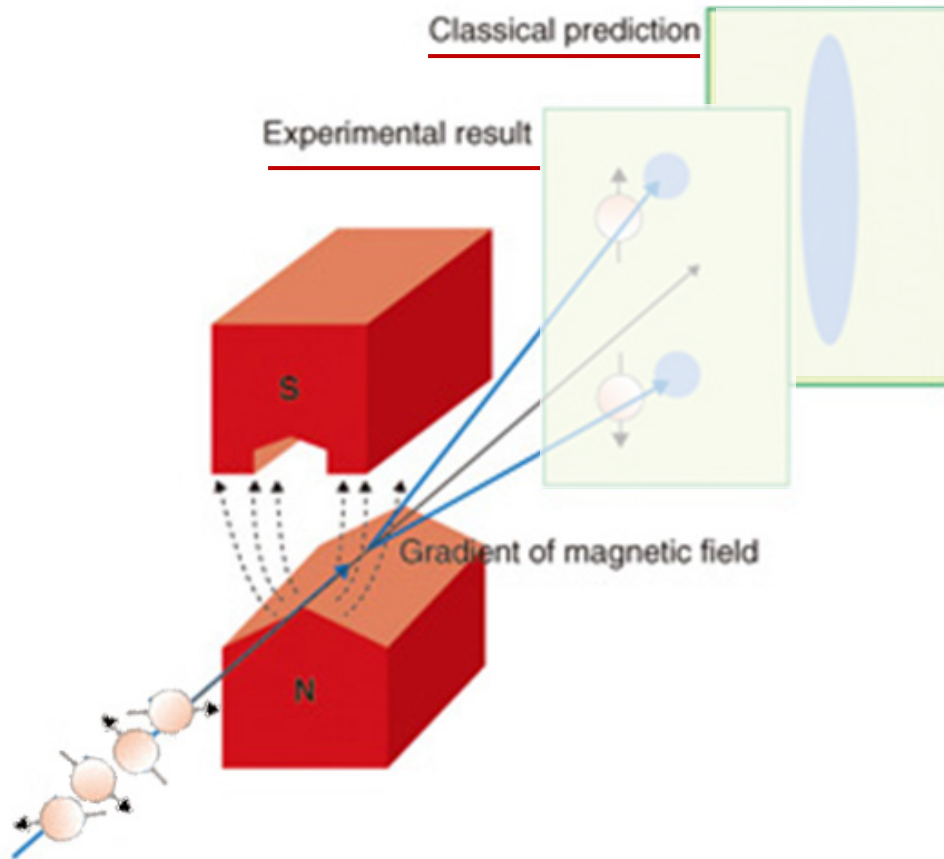
- Stern-Gerlach experiment (fig. 8-1 Silberberg)

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

# the 4<sup>th</sup> quantum number: spin

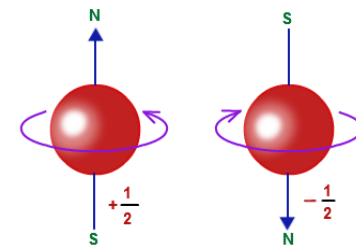


[https://www.ntt-review.jp/archive/ntttechnical.php?contents=ntr201209fa4\\_s.html](https://www.ntt-review.jp/archive/ntttechnical.php?contents=ntr201209fa4_s.html)

the electron has two possible spin states with spin quantum numbers

$$m_s = +\frac{1}{2} \text{ or } m_s = -\frac{1}{2}$$

*spin up and spin down*

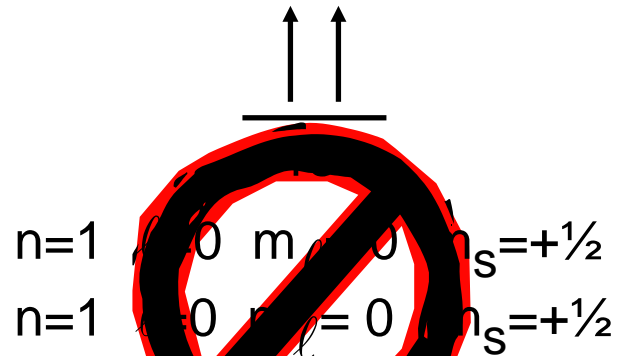
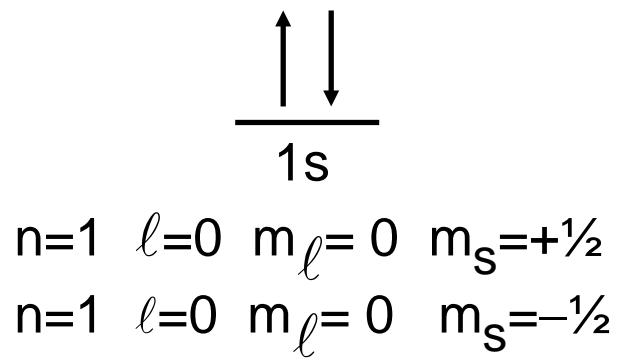


<http://www.quantum-field-theory.net/discovery-electron-spin/>

# Pauli exclusion principle (PEP) (sec 12.10)

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no two electrons can have the same four quantum numbers:



He, Li, Be, B, C, N, O, F, Ne .....

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



- 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.

**VOILA**

		Representative Elements		<i>d</i> -Transition Elements										Representative Elements					Noble Gases		
		IA <i>ns</i> <sup>1</sup>	Group numbers 2A <i>ns</i> <sup>2</sup>											3A <i>ns</i> <sup>2</sup> <i>np</i> <sup>1</sup>	4A <i>ns</i> <sup>2</sup> <i>np</i> <sup>2</sup>	5A <i>ns</i> <sup>2</sup> <i>np</i> <sup>3</sup>	6A <i>ns</i> <sup>2</sup> <i>np</i> <sup>4</sup>	7A <i>ns</i> <sup>2</sup> <i>np</i> <sup>5</sup>	8A <i>ns</i> <sup>2</sup> <i>np</i> <sup>6</sup>		
1	1	H <i>1s</i> <sup>1</sup>	2A																	2	He <i>1s</i> <sup>2</sup>
2	3	Li <i>2s</i> <sup>1</sup>	4	Be <i>2s</i> <sup>2</sup>											5	6	7	8	9	10	
															B <i>2s</i> <sup>2</sup> <i>2p</i> <sup>1</sup>	C <i>2s</i> <sup>2</sup> <i>2p</i> <sup>2</sup>	N <i>2s</i> <sup>2</sup> <i>2p</i> <sup>3</sup>	O <i>2s</i> <sup>2</sup> <i>2p</i> <sup>4</sup>	F <i>2s</i> <sup>2</sup> <i>2p</i> <sup>5</sup>	Ne <i>2s</i> <sup>2</sup> <i>2p</i> <sup>6</sup>	
3	11	Na <i>3s</i> <sup>1</sup>	12	Mg <i>3s</i> <sup>2</sup>											13	14	15	16	17	18	
															Al <i>3s</i> <sup>2</sup> <i>3p</i> <sup>1</sup>	Si <i>3s</i> <sup>2</sup> <i>3p</i> <sup>2</sup>	P <i>3s</i> <sup>2</sup> <i>3p</i> <sup>3</sup>	S <i>3s</i> <sup>2</sup> <i>3p</i> <sup>4</sup>	Cl <i>3s</i> <sup>2</sup> <i>3p</i> <sup>5</sup>	Ar <i>3s</i> <sup>2</sup> <i>3p</i> <sup>6</sup>	
4	19	K <i>4s</i> <sup>1</sup>	20	Ca <i>4s</i> <sup>2</sup>	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
					Sc <i>4s</i> <sup>2</sup> <i>3d</i> <sup>1</sup>	Ti <i>4s</i> <sup>2</sup> <i>3d</i> <sup>2</sup>	V <i>4s</i> <sup>2</sup> <i>3d</i> <sup>3</sup>	Cr <i>4s</i> <sup>1</sup> <i>3d</i> <sup>5</sup>	Mn <i>4s</i> <sup>2</sup> <i>3d</i> <sup>5</sup>	Fe <i>4s</i> <sup>2</sup> <i>3d</i> <sup>6</sup>	Co <i>4s</i> <sup>2</sup> <i>3d</i> <sup>7</sup>	Ni <i>4s</i> <sup>2</sup> <i>3d</i> <sup>8</sup>	Cu <i>4s</i> <sup>1</sup> <i>3d</i> <sup>10</sup>	Zn <i>4s</i> <sup>2</sup> <i>3d</i> <sup>10</sup>	Ga <i>4s</i> <sup>2</sup> <i>4p</i> <sup>1</sup>	Ge <i>4s</i> <sup>2</sup> <i>4p</i> <sup>2</sup>	As <i>4s</i> <sup>2</sup> <i>4p</i> <sup>3</sup>	Se <i>4s</i> <sup>2</sup> <i>4p</i> <sup>4</sup>	Br <i>4s</i> <sup>2</sup> <i>4p</i> <sup>5</sup>	Kr <i>4s</i> <sup>2</sup> <i>4p</i> <sup>6</sup>	
5	37	Rb <i>5s</i> <sup>1</sup>	38	Sr <i>5s</i> <sup>2</sup>	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
					Y <i>5s</i> <sup>2</sup> <i>4d</i> <sup>1</sup>	Zr <i>5s</i> <sup>2</sup> <i>4d</i> <sup>2</sup>	Nb <i>5s</i> <sup>1</sup> <i>4d</i> <sup>4</sup>	Mo <i>5s</i> <sup>1</sup> <i>4d</i> <sup>5</sup>	Tc <i>5s</i> <sup>1</sup> <i>4d</i> <sup>5</sup>	Ru <i>5s</i> <sup>1</sup> <i>4d</i> <sup>7</sup>	Rh <i>5s</i> <sup>1</sup> <i>4d</i> <sup>8</sup>	Pd <i>4d</i> <sup>10</sup>	Ag <i>5s</i> <sup>1</sup> <i>4d</i> <sup>10</sup>	Cd <i>5s</i> <sup>2</sup> <i>4d</i> <sup>10</sup>	In <i>5s</i> <sup>2</sup> <i>5p</i> <sup>1</sup>	Sn <i>5s</i> <sup>2</sup> <i>5p</i> <sup>2</sup>	Sb <i>5s</i> <sup>2</sup> <i>5p</i> <sup>3</sup>	Te <i>5s</i> <sup>2</sup> <i>5p</i> <sup>4</sup>	I <i>5s</i> <sup>2</sup> <i>5p</i> <sup>5</sup>	Xe <i>5s</i> <sup>2</sup> <i>5p</i> <sup>6</sup>	
6	55	Cs <i>6s</i> <sup>1</sup>	56	Ba <i>6s</i> <sup>2</sup>	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
					La* <i>6s</i> <sup>2</sup> <i>5d</i> <sup>1</sup>	Hf <i>6s</i> <sup>2</sup> <i>5d</i> <sup>2</sup>	Ta <i>6s</i> <sup>2</sup> <i>5d</i> <sup>3</sup>	W <i>6s</i> <sup>2</sup> <i>5d</i> <sup>4</sup>	Re <i>6s</i> <sup>2</sup> <i>5d</i> <sup>5</sup>	Os <i>6s</i> <sup>2</sup> <i>5d</i> <sup>6</sup>	Ir <i>6s</i> <sup>2</sup> <i>5d</i> <sup>7</sup>	Pt <i>6s</i> <sup>1</sup> <i>5d</i> <sup>9</sup>	Au <i>6s</i> <sup>1</sup> <i>5d</i> <sup>10</sup>	Hg <i>6s</i> <sup>2</sup> <i>5d</i> <sup>10</sup>	Tl <i>6s</i> <sup>2</sup> <i>6p</i> <sup>1</sup>	Pb <i>6s</i> <sup>2</sup> <i>6p</i> <sup>2</sup>	Bi <i>6s</i> <sup>2</sup> <i>6p</i> <sup>3</sup>	Po <i>6s</i> <sup>2</sup> <i>6p</i> <sup>4</sup>	At <i>6s</i> <sup>2</sup> <i>6p</i> <sup>5</sup>	Rn <i>6s</i> <sup>2</sup> <i>6p</i> <sup>6</sup>	
7	87	Fr <i>7s</i> <sup>1</sup>	88	Ra <i>7s</i> <sup>2</sup>	89	104	105	106	107	108	109	110	111	112	114						
					Ac** <i>7s</i> <sup>2</sup> <i>6d</i> <sup>1</sup>	Rf <i>7s</i> <sup>2</sup> <i>6d</i> <sup>2</sup>	Db <i>7s</i> <sup>2</sup> <i>6d</i> <sup>3</sup>	Sg <i>7s</i> <sup>2</sup> <i>6d</i> <sup>4</sup>	Bh <i>7s</i> <sup>2</sup> <i>6d</i> <sup>5</sup>	Hs <i>7s</i> <sup>2</sup> <i>6d</i> <sup>6</sup>	Mt <i>7s</i> <sup>2</sup> <i>6d</i> <sup>7</sup>	Ds <i>7s</i> <sup>2</sup> <i>6d</i> <sup>8</sup>	Uuu <i>7s</i> <sup>1</sup> <i>6d</i> <sup>10</sup>	Uub <i>7s</i> <sup>2</sup> <i>6d</i> <sup>10</sup>	Uuq <i>7s</i> <sup>2</sup> <i>7p</i> <sup>2</sup>						

		<i>f</i> -Transition Elements												
*Lanthanides	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce <i>6s</i> <sup>2</sup> <i>4f</i> <sup>1</sup> <i>5d</i> <sup>1</sup>	Pr <i>6s</i> <sup>2</sup> <i>4f</i> <sup>3</sup> <i>5d</i> <sup>0</sup>	Nd <i>6s</i> <sup>2</sup> <i>4f</i> <sup>4</sup> <i>5d</i> <sup>0</sup>	Pm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>5</sup> <i>5d</i> <sup>0</sup>	Sm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>6</sup> <i>5d</i> <sup>0</sup>	Eu <i>6s</i> <sup>2</sup> <i>4f</i> <sup>7</sup> <i>5d</i> <sup>0</sup>	Gd <i>6s</i> <sup>2</sup> <i>4f</i> <sup>7</sup> <i>5d</i> <sup>1</sup>	Tb <i>6s</i> <sup>2</sup> <i>4f</i> <sup>9</sup> <i>5d</i> <sup>0</sup>	Dy <i>6s</i> <sup>2</sup> <i>4f</i> <sup>10</sup> <i>5d</i> <sup>0</sup>	Ho <i>6s</i> <sup>2</sup> <i>4f</i> <sup>11</sup> <i>5d</i> <sup>0</sup>	Er <i>6s</i> <sup>2</sup> <i>4f</i> <sup>12</sup> <i>5d</i> <sup>0</sup>	Tm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>13</sup> <i>5d</i> <sup>0</sup>	Yb <i>6s</i> <sup>2</sup> <i>4f</i> <sup>14</sup> <i>5d</i> <sup>0</sup>	Lu <i>6s</i> <sup>2</sup> <i>4f</i> <sup>14</sup> <i>5d</i> <sup>1</sup>
**Actinides	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>2</sup>	Pa <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>1</sup>	U <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>1</sup>	Np <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Pu <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Am <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Cm <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Bk <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Cf <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Es <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Fm <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Md <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	No <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>0</sup>	Lr <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>1</sup>

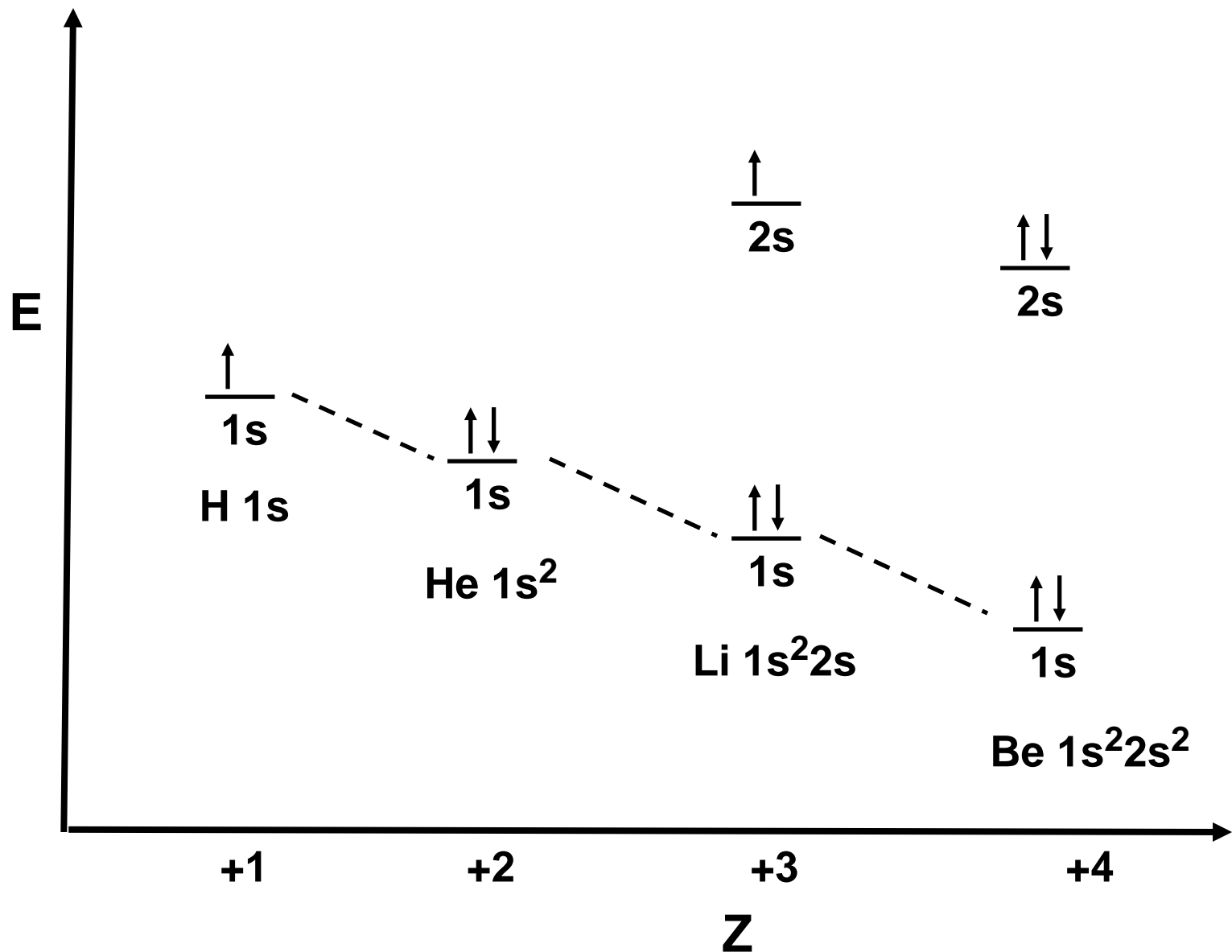
**electronic configuration:** specification of which orbitals the electrons occupy in an atom (or molecule) [*and possibly the spins of electrons*]

e.g. for H:  $1s$  or  $\begin{array}{c} \uparrow \\ \text{---} \\ 1s \end{array}$

He:  $1s^2$  or  $\begin{array}{c} \uparrow\downarrow \\ \text{---} \\ 1s \end{array}$

C:  $1s^2 2s^2 2p^2$   $\begin{array}{c} \uparrow \quad \uparrow \quad \text{---} \\ \text{---} \\ 2p \end{array}$

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



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

**n and Z**

$$E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{Z^2}{n^2} = -(2.18 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2}$$

$$\bar{r} \approx (5.29 \times 10^{-11} \text{ m}) \frac{n^2}{Z}$$

- Holds **EXACTLY** for 1-electron atoms and ions:  
H, He<sup>+</sup>, Li<sup>2+</sup>, Be<sup>3+</sup>, ...  
*Here Z is “regular” nuclear charge with Z=1, 2, 3, 4,*

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

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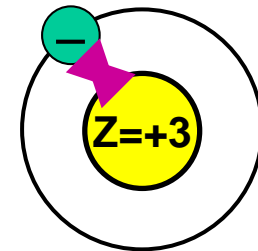
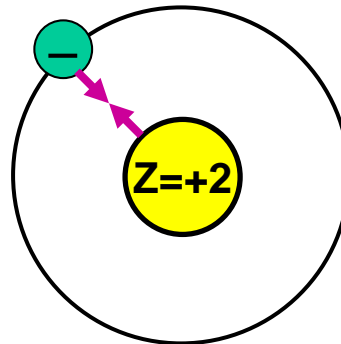
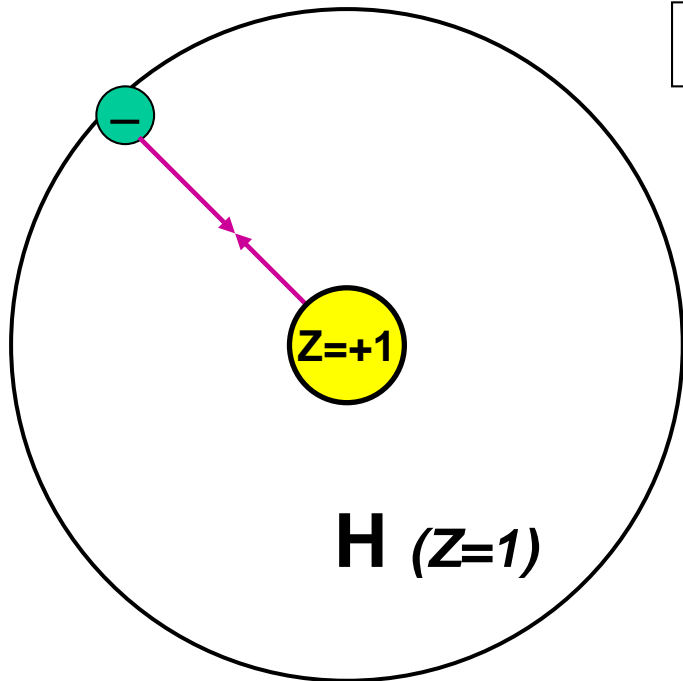
- ionization energy (**IE**) : the energy required to remove an electron from an atom, ion, or molecule in the gas phase
- $X(g) + \text{IE} \rightarrow X^+(g) + e^-$  (absorbs energy IE:  
*endothermic, + sign for IE*)
- $\text{IE}_n$  for state  $n$  is energy difference between state  $n$  and state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

$$(\text{I.E.})_n = (E_\infty - E_n) = -E_n = + (2.18 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2}$$

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

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

all 1s electrons ( $n=1$ )



$$E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{Z^2}{n^2} = -(2.18 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2}$$

"Bohr" radius in gas phase

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

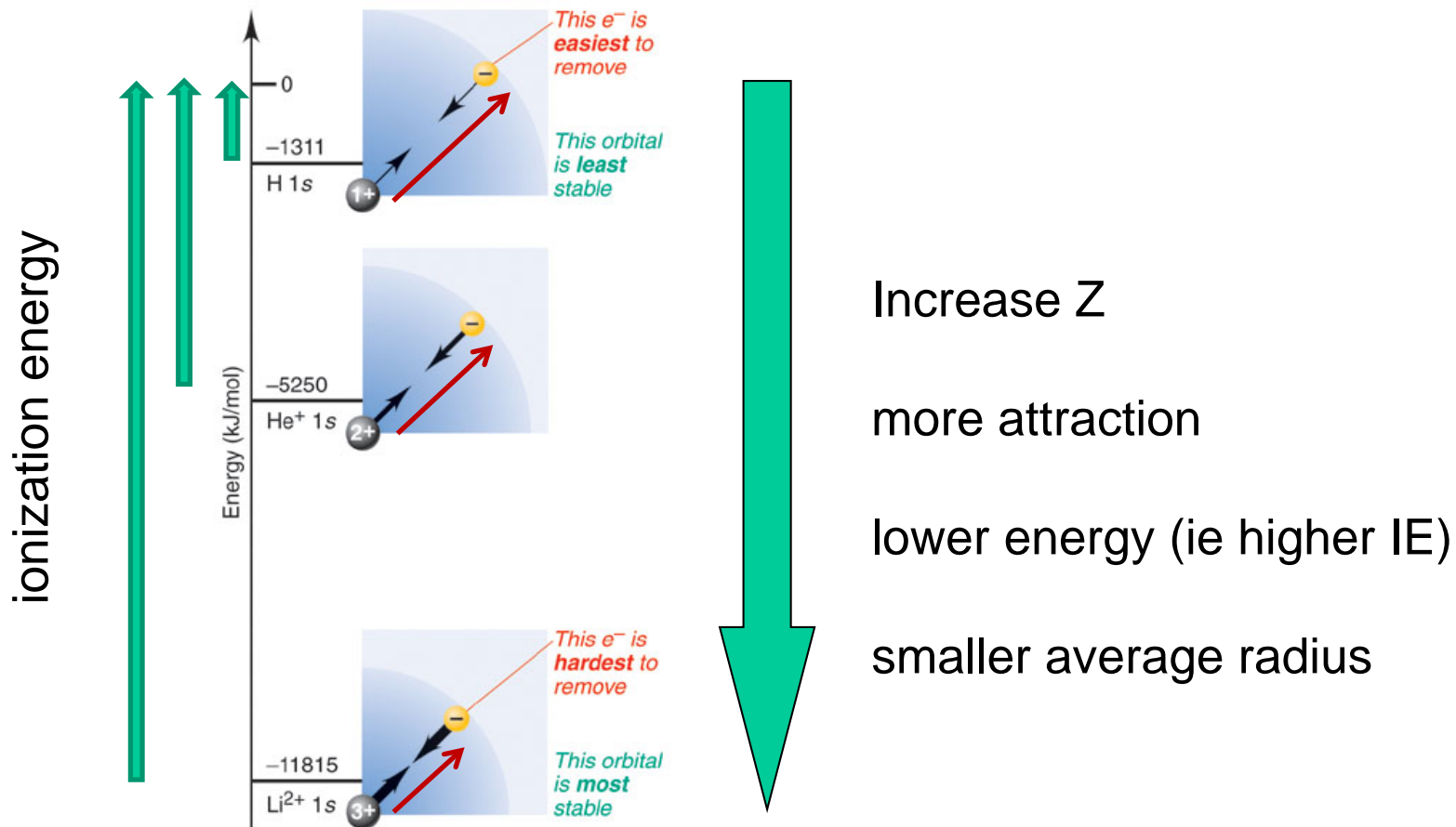
increase  $Z$

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

# Silberberg Figure 8.3

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

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## Important factoids in Understanding Effective Nuclear Charge



- Energy dependence on  $n$  and  $Z_{\text{eff}}$

$$E_n \approx - (2.18 \times 10^{-18} \text{ J}) \frac{Z_{\text{eff}}^2}{n^2}$$

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

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

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

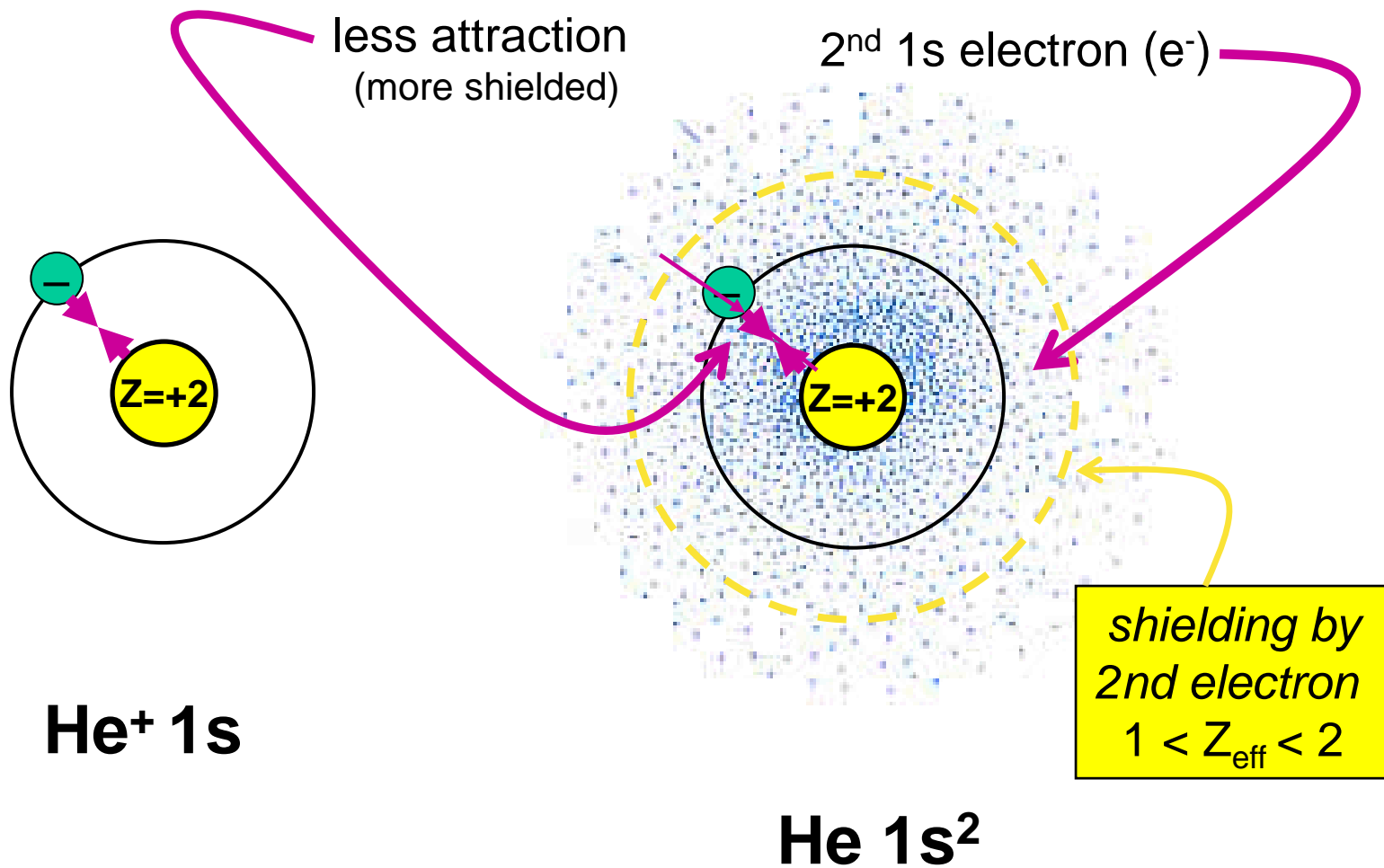
1s electron 'feels' full  $Z=+2$  nuclear attraction

- electrons in same shell:



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

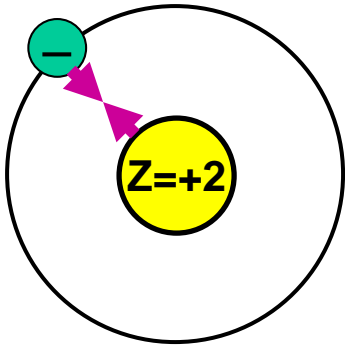
# *He<sup>+</sup> vs He (what positive charge does a 1s electron 'see' ?)*



more shielding → lower  $Z_{\text{eff}}$  → larger average radius

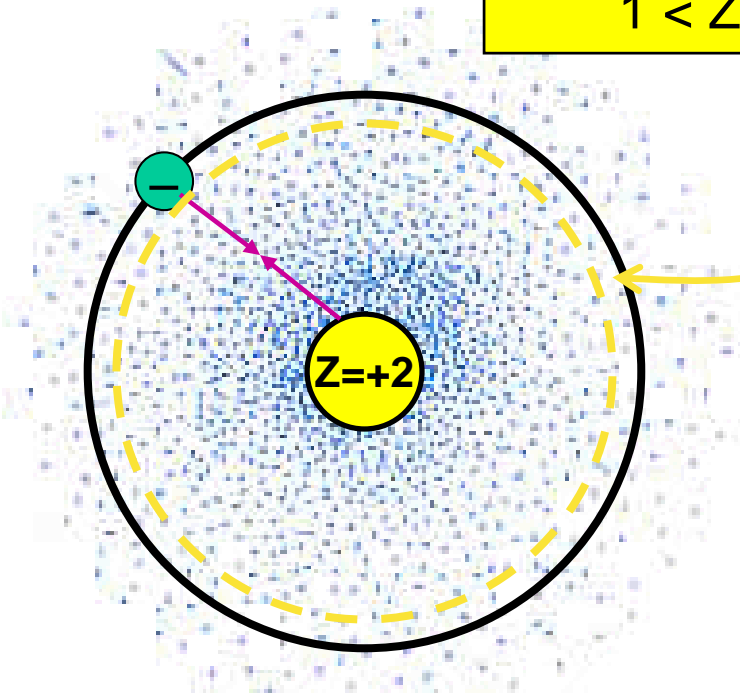
*He<sup>+</sup> vs He (what **net** positive charge does a 1s electron 'see' ?)*

no shielding  $Z_{\text{eff}} = 2$



**He<sup>+</sup> 1s**

shielding of electron  
by 2nd 1s electron  
 $1 < Z_{\text{eff}} < 2$



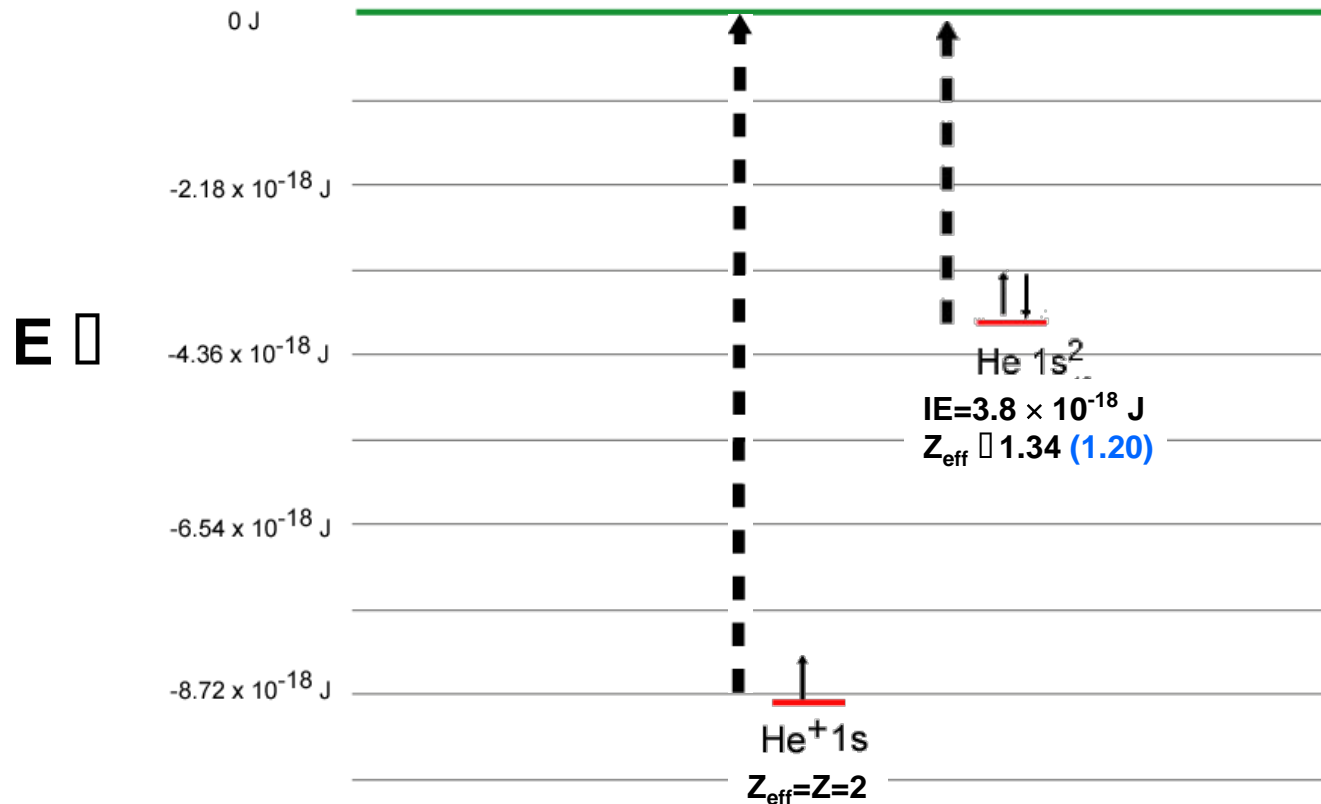
**He 1s<sup>2</sup>**

lower  $Z_{\text{eff}}$  → larger average radius  
lower  $Z_{\text{eff}}$  → lower attractive forces

# Energy of He 1s<sup>2</sup> vs He<sup>+</sup> 1s (HO fig 12.2)

## Z<sub>eff</sub> and Ionization Energies

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



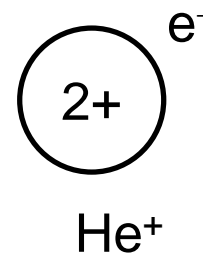
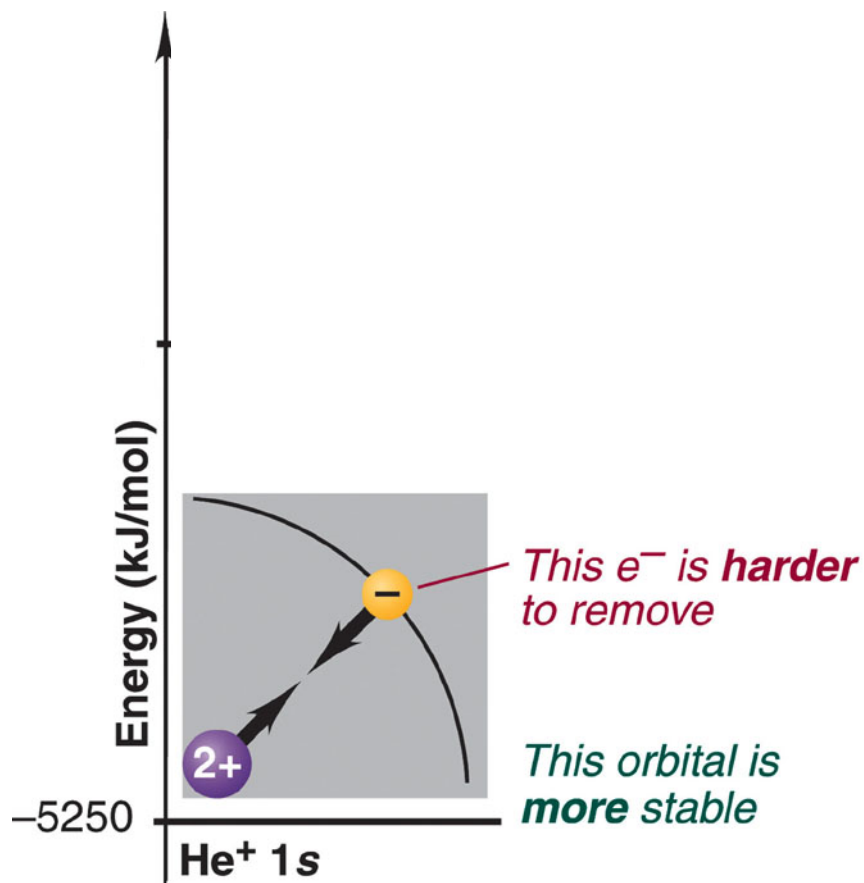
$$IE \approx (2.18 \times 10^{-18} \text{ J}) \frac{Z_{\text{eff}}^2}{n^2}$$

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

*this is approximate way to calculate Z<sub>eff</sub>; other techniques give slightly different numbers*

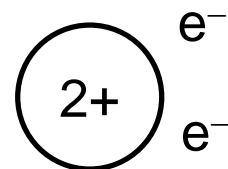
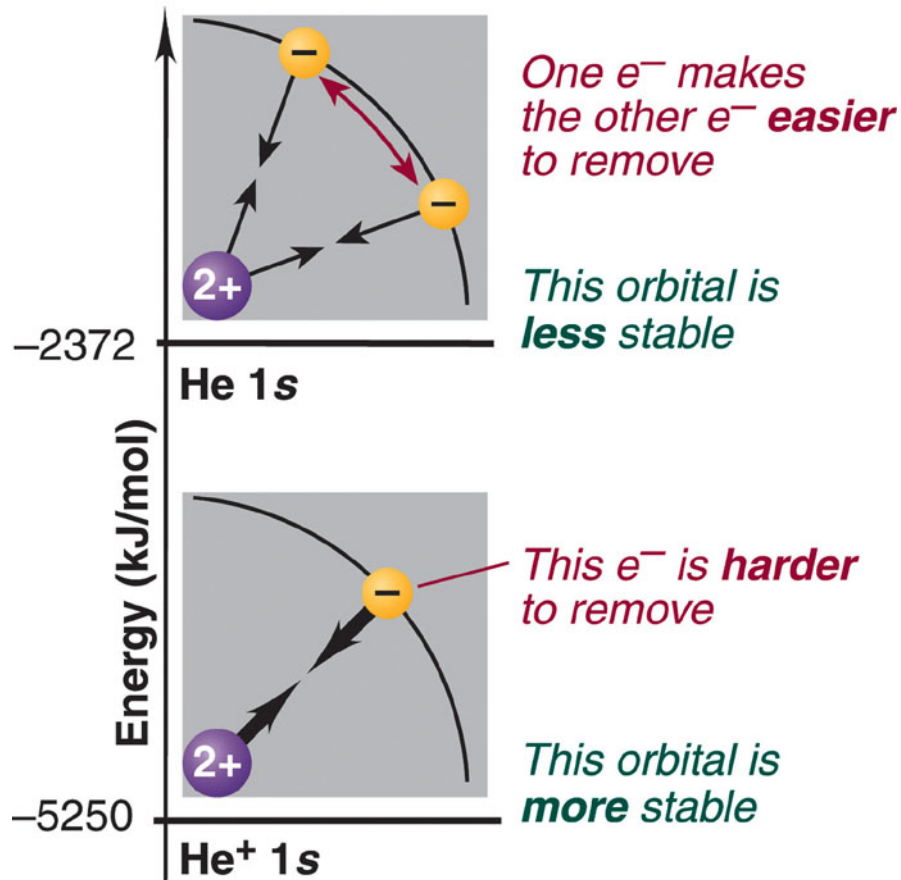
energy of  $\text{He } 1s^2$  vs  $\text{He}^+ 1s$  (same shell shielding)  
Zumdahl (p. 558-9)

---

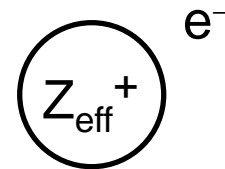


Silberberg figure 8.4A: energy of  $\text{He } 1s^2$  vs  $\text{He}^+ 1s$   
 (same shell shielding) Zumdahl (p. 556-8) [558-559]<sub>7th</sub>

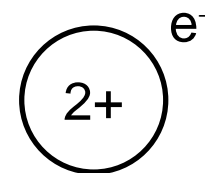
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actual He atom



Zumdahl's 'hypothetical' He atom



$\text{He}^+$

**what about shielding if the electrons are in different shells**

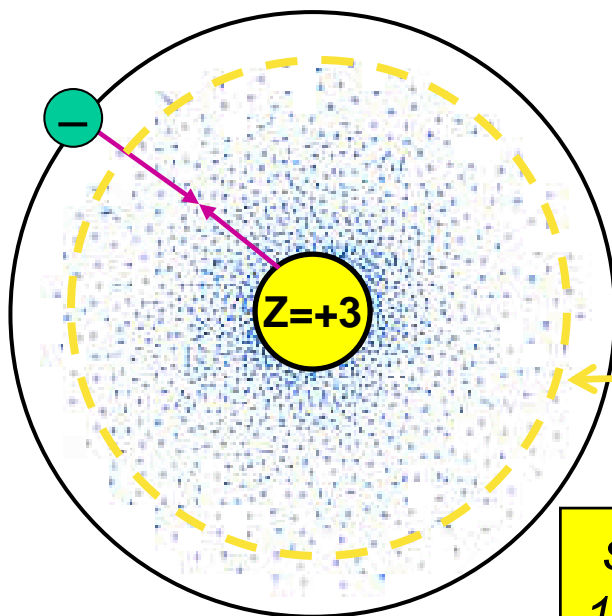


*shielding the 2s electron* 

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

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

2s electron



$$\mathbf{IE}_{\text{experimental}} = \mathbf{0.86} \times \mathbf{10^{-18} \text{ J}}$$

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

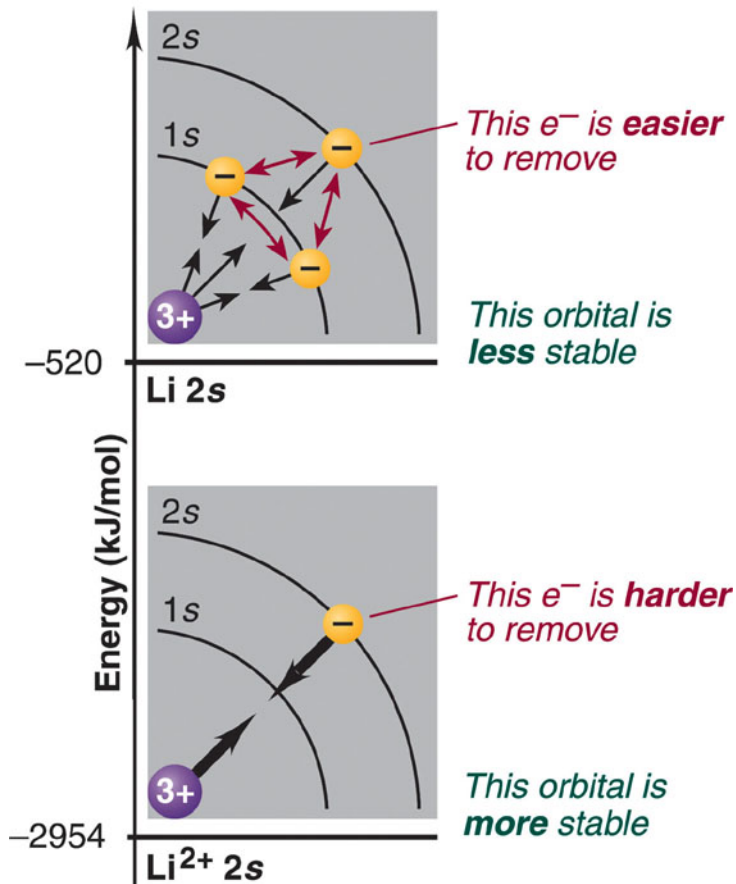
shielding by  
 $1s^2$  electrons  
 $Z_{\text{eff}} \approx 1.26$

**Li  $1s^2 2s$**



# figure 8.4 B (Silb) shielding by inner shell electrons

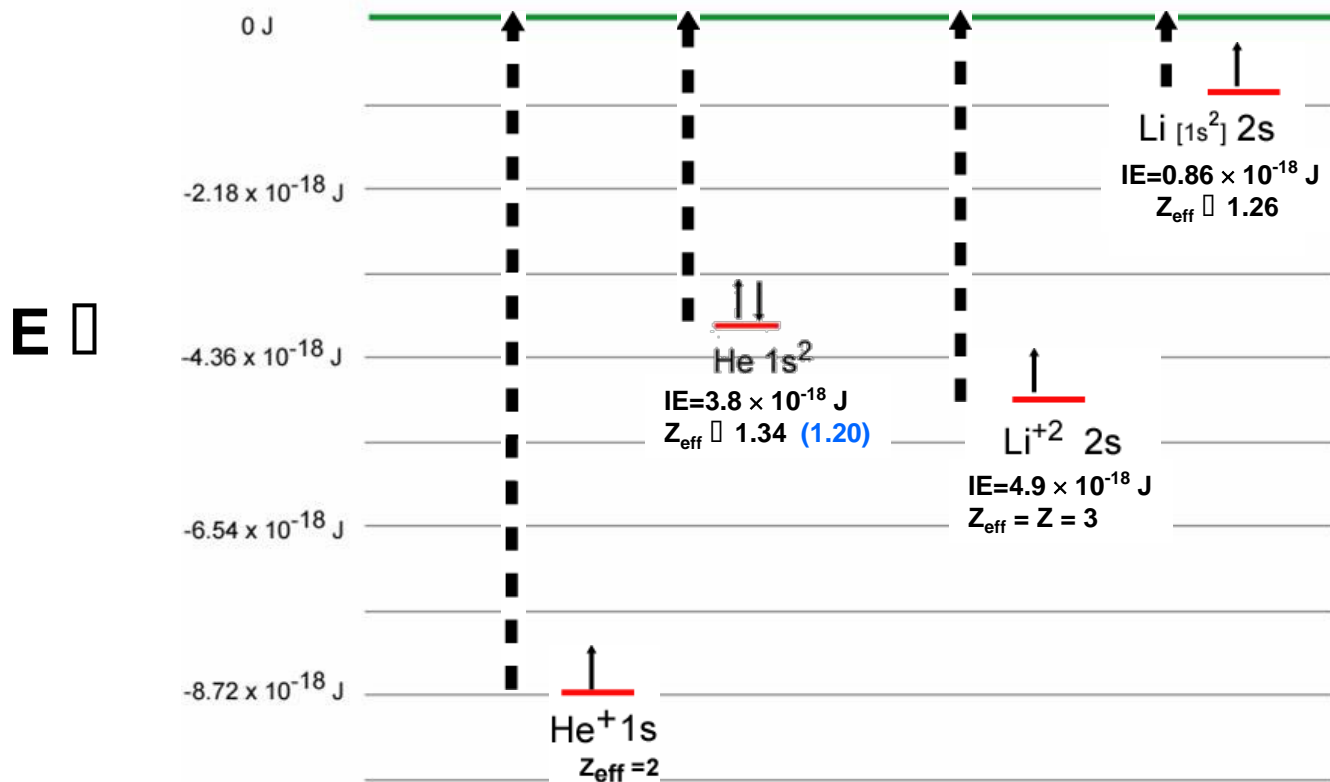
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# Energy of $\text{Li}^{2+} 2s$ vs $\text{Li} [1s^2] 2s$ (HO Fig. 12.3)

$Z_{\text{eff}}$  and Ionization Energies

$$Z_{\text{eff}} (\text{Li}^{2+} 2s) > Z_{\text{eff}} (\text{Li} [1s^2] 2s)$$




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

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

## same shell shielding He $1s^2$ vs inner shell shielding Li $1s^2 2s$

---

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 Li  $1s^2 2s$

---

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

He :  $Z_{eff}(1s) \approx 1.34 = +2 - \text{shielding of other } 1s \text{ electron}$   
shielding of **other 1s electron = 0.66**

Li :  $Z_{eff}(2s) \approx 1.26 = +3 - \text{shielding of two } 1s \text{ electrons}$   
shielding of each inner shell 1s electron =  $\frac{1.74}{2} = \mathbf{0.87}$

DONE FOR NOW !!



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

- Stern-Gerlach electron spin  $+\frac{1}{2}$  and  $-\frac{1}{2}$
- Pauli Exclusion Principle (PEP)
- effective nuclear charge:  $Z_{\text{eff}}$ 
  - $+Z_{\text{nuclear charge}}$  — repulsion (shielding) by other electrons
  - shielding greater from electron in inner shell than electron in same shell [from electrons 'inside' or closer to nucleus]

- $$E_n \approx -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{Z_{\text{eff}}^2}{n^2} = -(2.18 \times 10^{-18} \text{ J}) \frac{Z_{\text{eff}}^2}{n^2} \quad \bar{r} \approx (5.29 \times 10^{-11} \text{ m}) \frac{n^2}{Z_{\text{eff}}}$$

*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 ( $\text{He}^+$ ,  $\text{Li}^{2+}$  ...), a 2s and 2p orbital will have the .. **SAME** .. energy

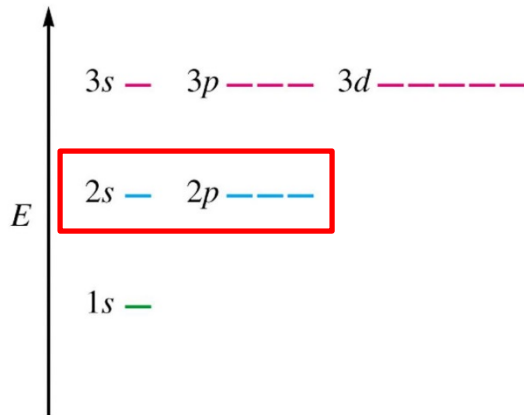


fig. 12.23 for 1-electron atoms and ions

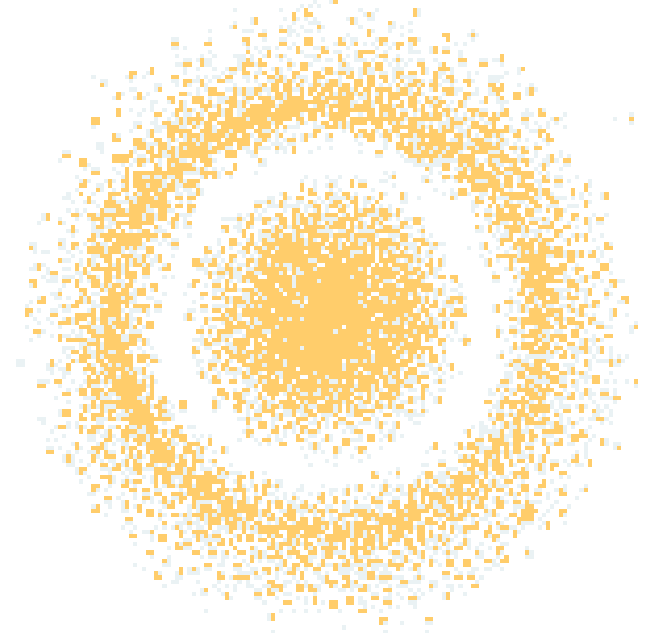
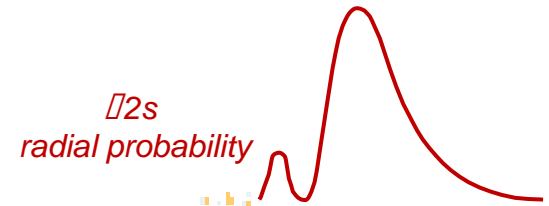
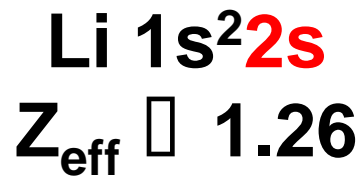
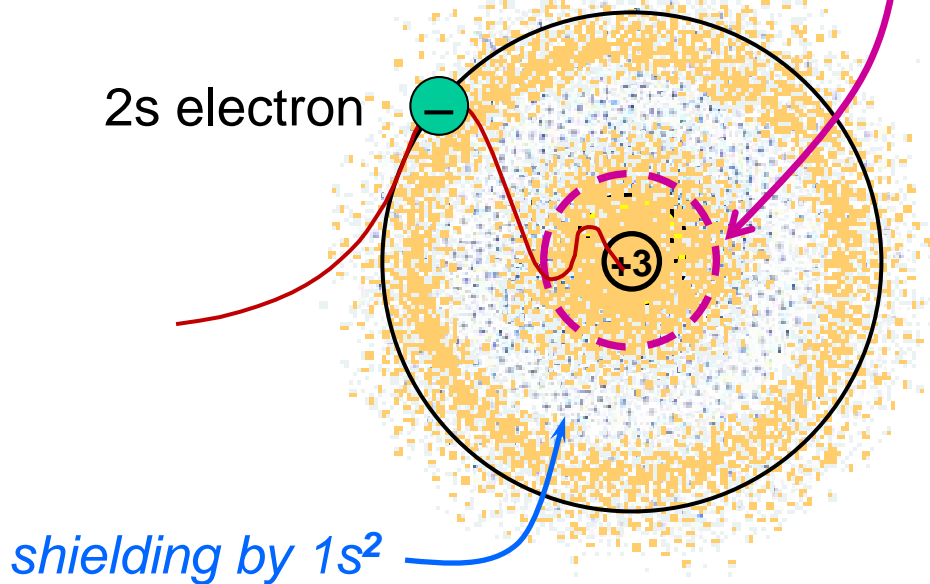
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**now  $Z_{\text{eff}}$**

**and the effect of penetration of inner shell  
electron density by electrons in the same  
shell (e.g. 2s electron vs 2p electron )**

$Z_{\text{eff}}$  for 2s vs 2p: 2p and 2s have SAME energy in 1-electron ion

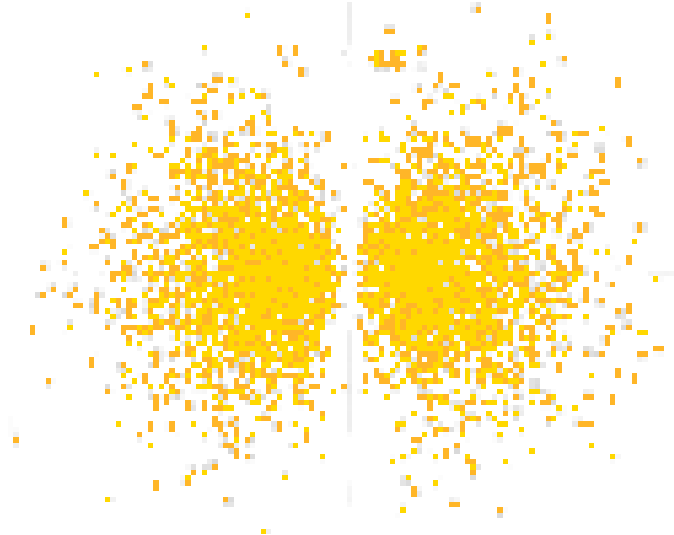
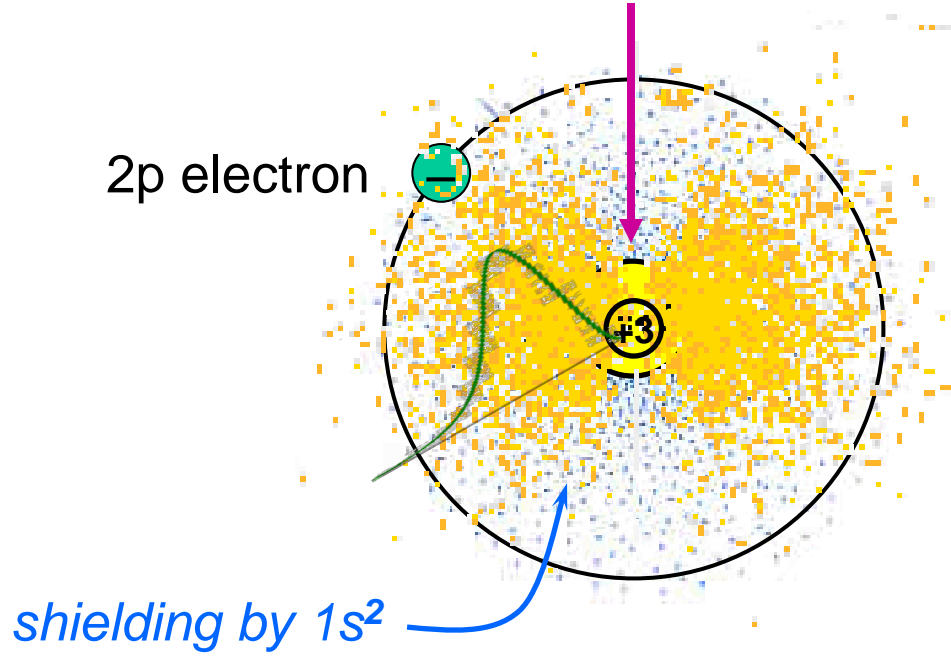
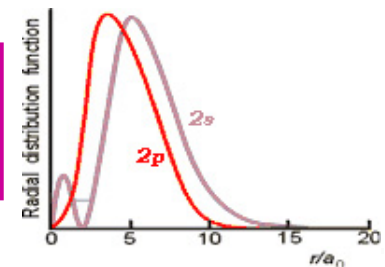
'penetration' by 2s electron  
of  $1s^2$  shielding  
GIVES INCREASED  $Z_{\text{eff}}$



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

# $Z_{\text{eff}}$ for 2s vs 2p

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



**Li  $1s^2 2p$**

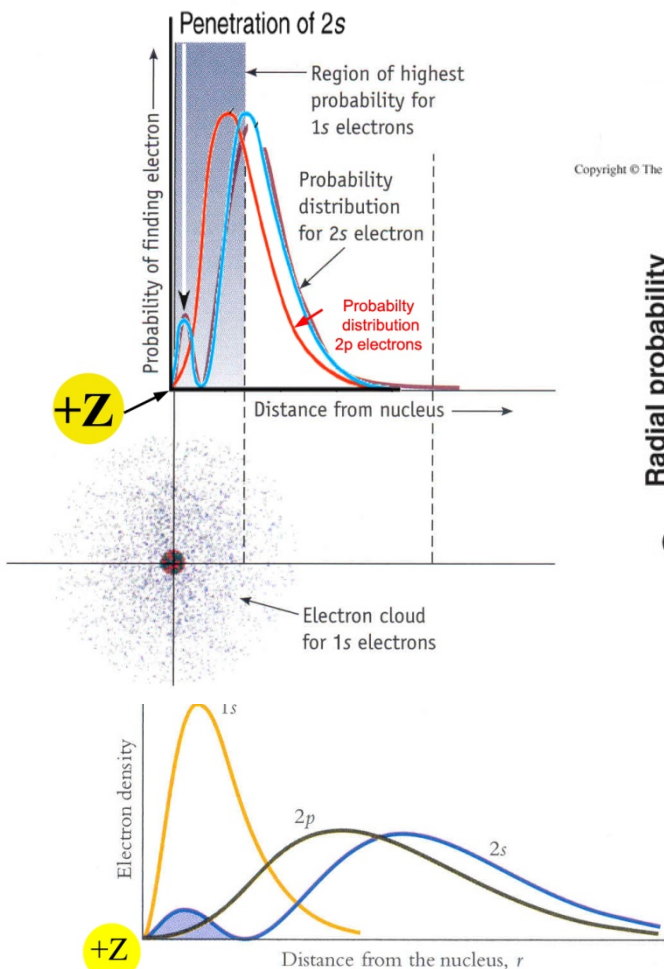
$$Z_{\text{eff}} \text{ for } 2s > Z_{\text{eff}} \text{ for } 2p$$
$$E_{2s} < E_{2p}$$

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

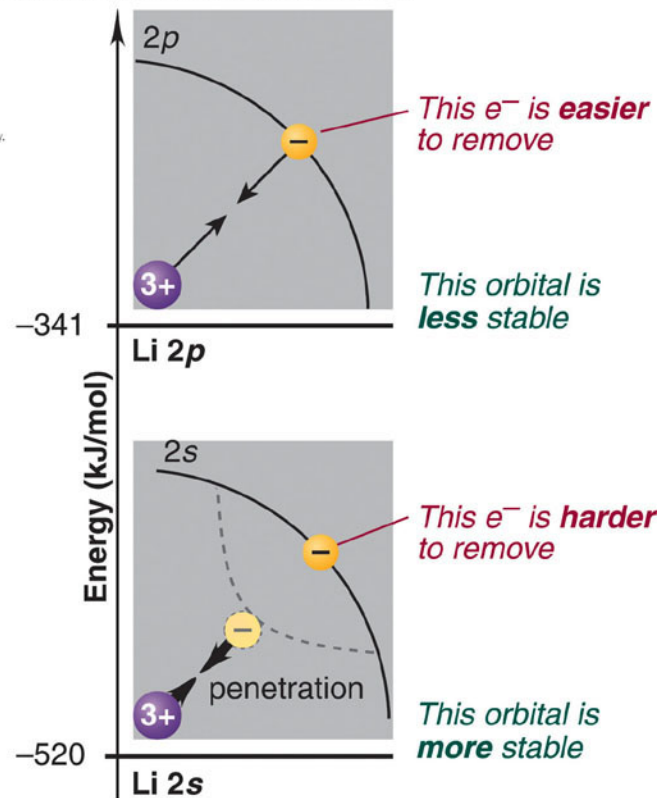
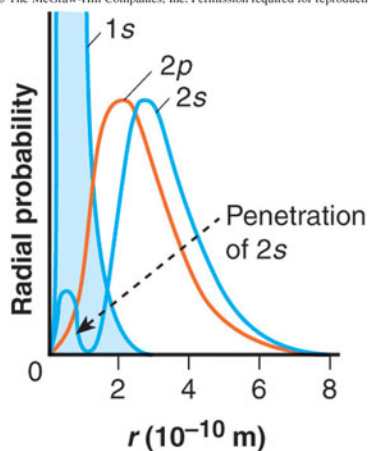


# $Z_{\text{eff}}$ for 2s vs 2p (handout fig. 12.4)

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**more penetration of inner shell electron density**



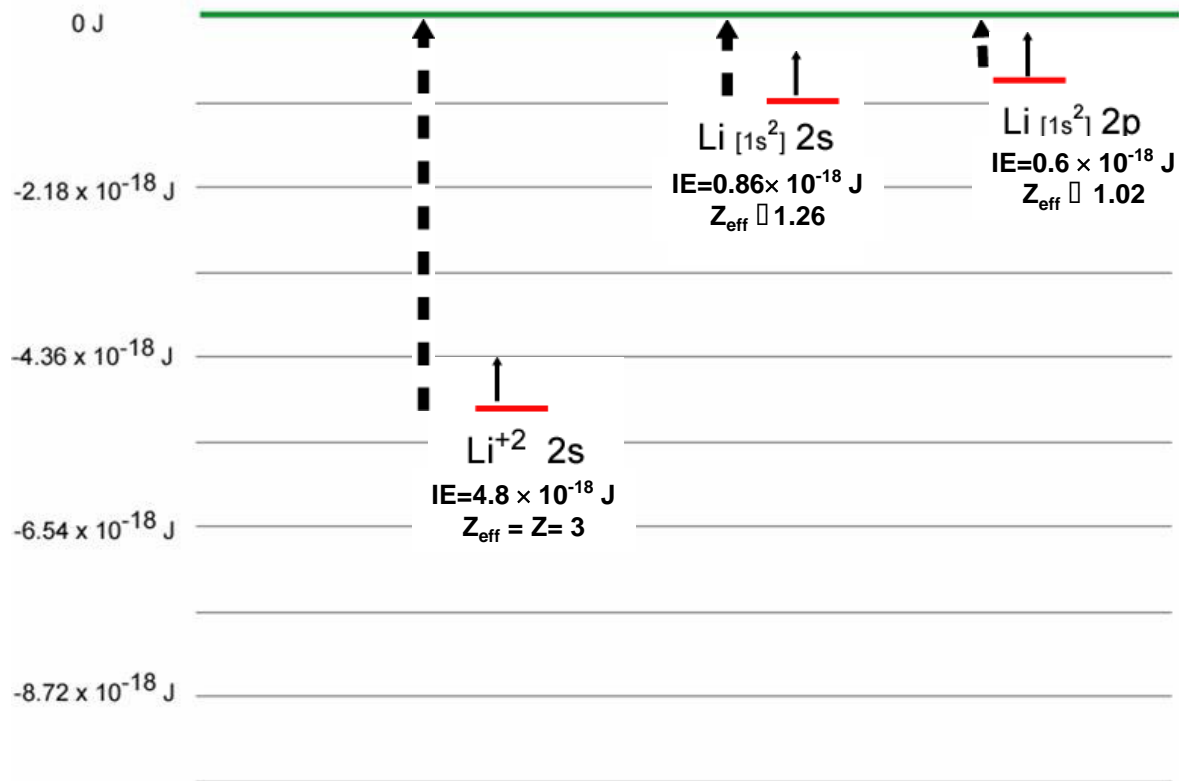
$$E_{2s} < E_{2p}$$




**electron see's more +Z and has greater  $Z_{\text{eff}}$**

# Energy of $\text{Li} [1s^2] 2s$ vs $\text{Li} [1s^2] 2p$ (HO Fig. 12.5): penetration

$Z_{\text{eff}}$  and Ionization Energies

$$Z_{\text{eff}} (\text{Li}[1s^2] 2s) > Z_{\text{eff}} (\text{Li}[1s^2]2p)$$



- **Configurations and valence-level orbital diagrams** 
- **Hund's rule** 
- **2<sup>nd</sup> row aufbau fig 8.8 (Si)** 





- Increasing  $Z_{\text{eff}}$  due to increasing penetration effects ([figure HO 12Z.6](#));  $\implies$

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

$$(E)_{3s} < (E)_{3p} < (E)_{3d}$$

- 4s vs 3d ( $Z_{\text{eff}}$  vs n)  $\implies$

- Orbital energy ordering [fig 8.6 \(Silb\)](#)  
[\(figure 8.13, Silb\)](#)  $\implies$

- **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” 

# unpaired electrons and magnetic properties (Gouy balance)

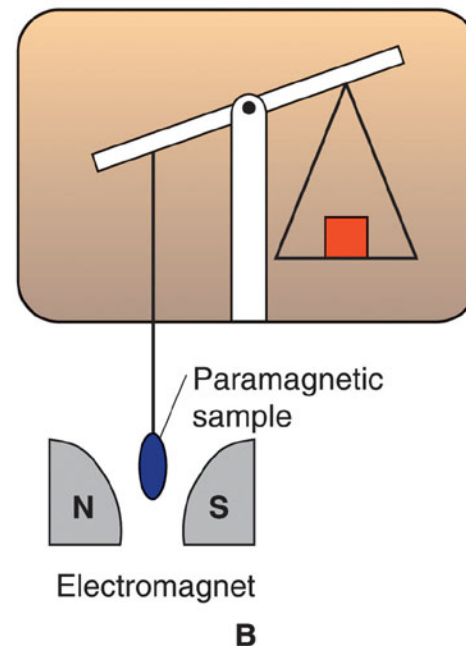
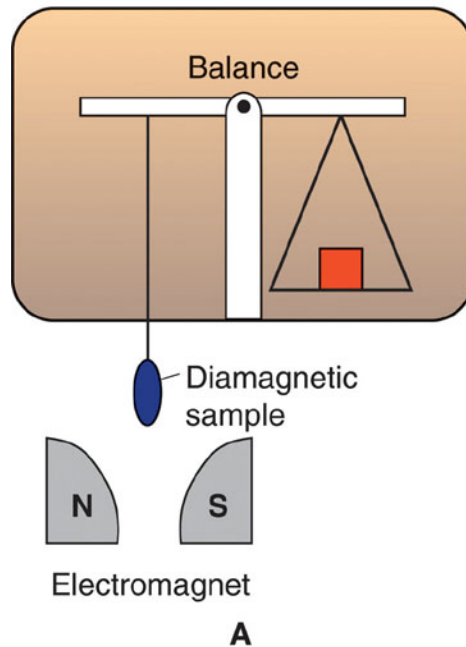
## Diamagnetic

- pushed out of magnet
- no unpaired electrons

## Paramagnetic

- pulled into magnet
- unpaired electrons

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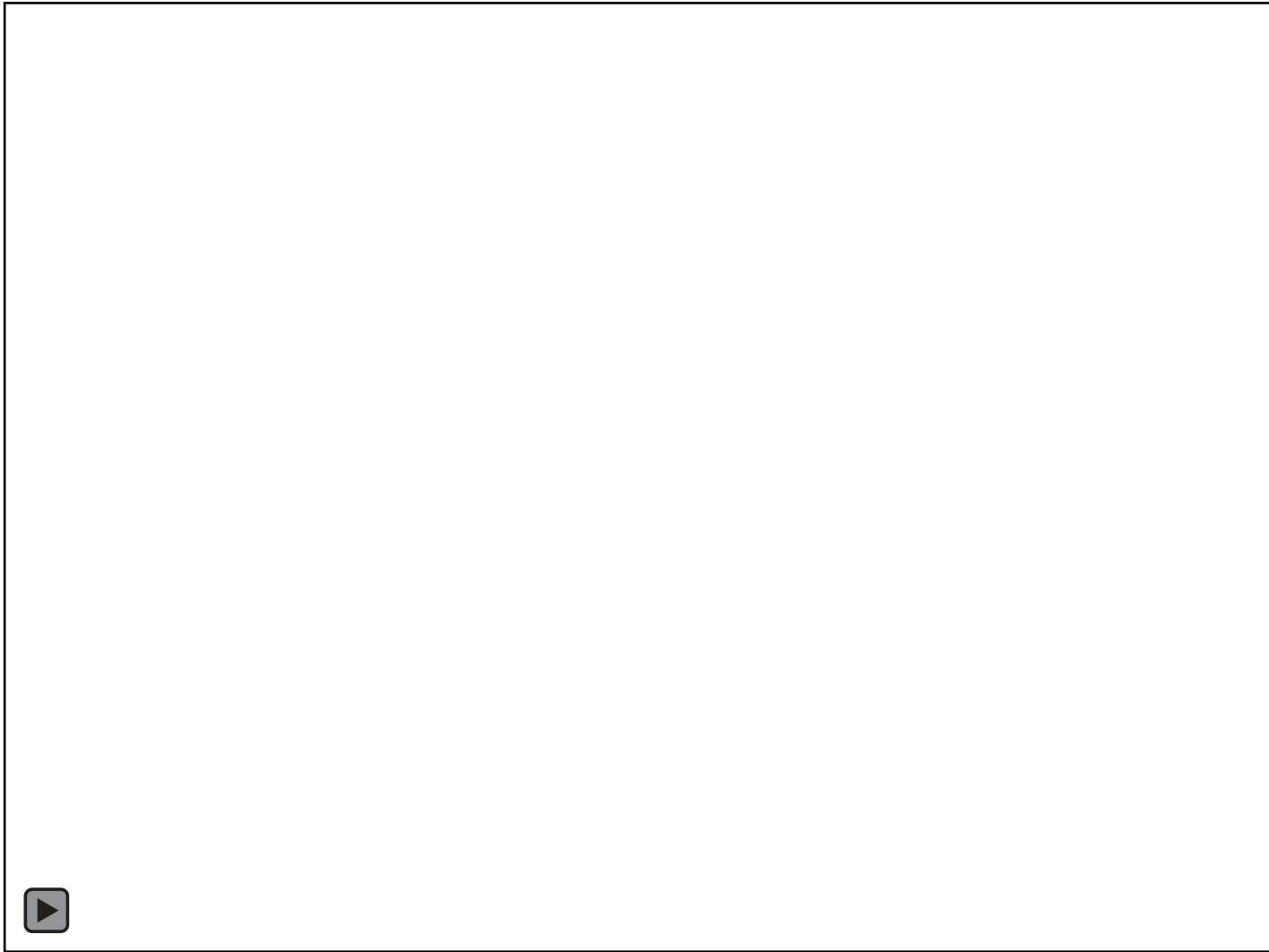
Gouy Balance

# Periodic Table



Given **PEP** and ordering of orbitals, we can build up the periodic table element by element, and deduce much about the chemical nature of the elements as they interact to form molecules.



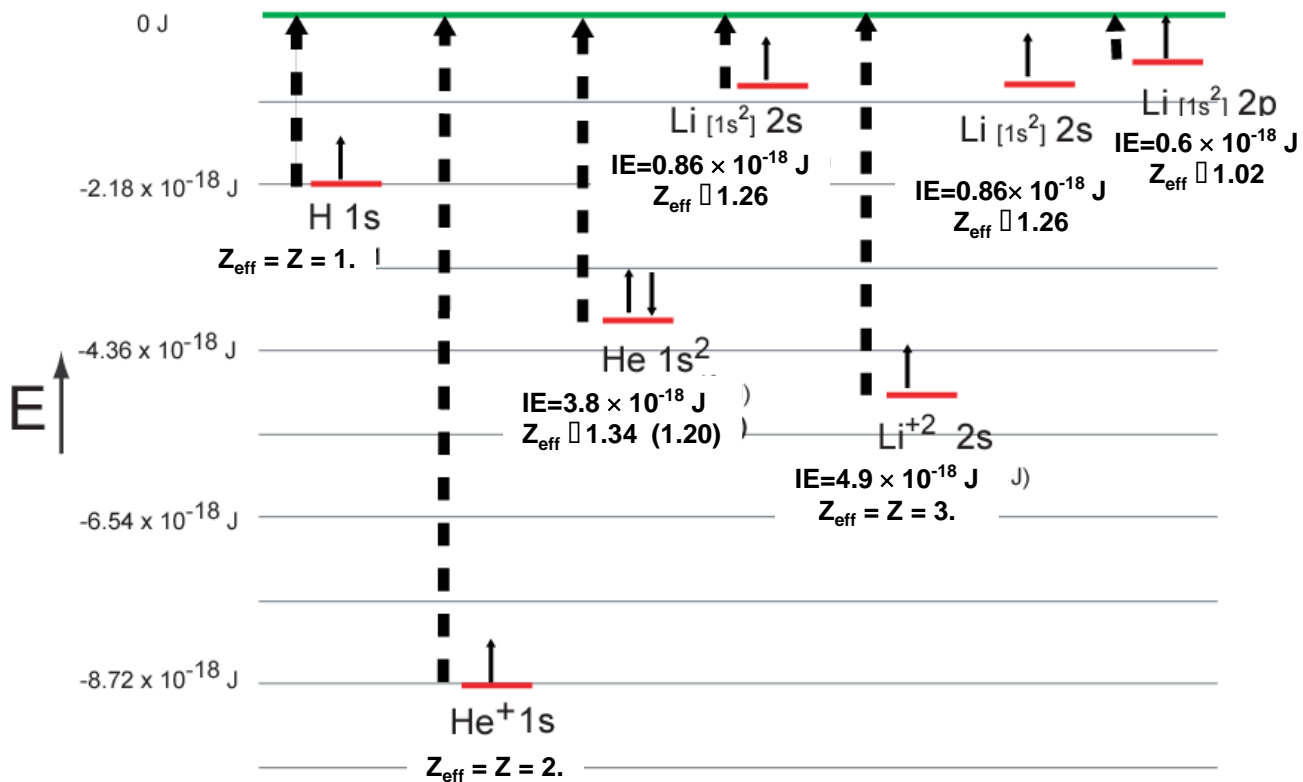




# $Z_{\text{eff}}$ and ionization potentials

## $Z_{\text{eff}}$ and Ionization Energies

Note: data refer to figures 8.3, 8.4, 8.5 Silberberg  
 IP in J/molecule = (IP in kJ/mol x 1000 J/kJ)/(6.022 x 10<sup>23</sup> molecules/mol)











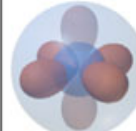
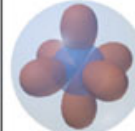
CONCLUSIONS:

$$Z_{\text{eff}}(\text{He}^+ 1s) > Z_{\text{eff}}(\text{He } 1s); \quad Z_{\text{eff}}(\text{Li } [1s^2] 2s) > Z_{\text{eff}}(\text{Li } [1s^2] 2p)$$

$$Z_{\text{eff}}(\text{Li}^{2+} 2s) > Z_{\text{eff}}(\text{Li } [1s^2] 2s);$$

# Silberberg figure 8.8

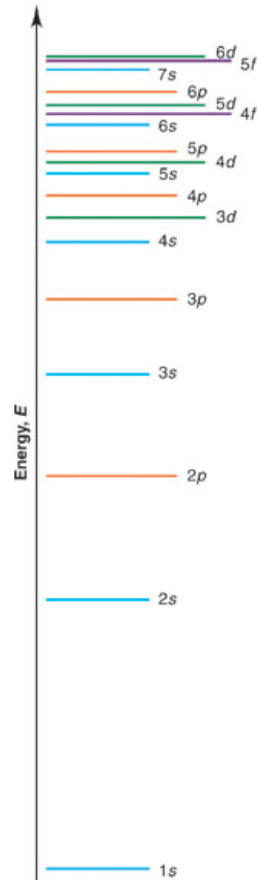
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	1A(1)		2A(2)	3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
Period 1	1 <b>H</b> $1s^1$ 								2 <b>He</b> $1s^2$ 
Period 2	3 <b>Li</b> $1s^2 2s^1$ 	4 <b>Be</b> $1s^2 2s^2$ 	5 <b>B</b> $1s^2 2s^2 2p^1$ 	6 <b>C</b> $1s^2 2s^2 2p^2$ 	7 <b>N</b> $1s^2 2s^2 2p^3$ 	8 <b>O</b> $1s^2 2s^2 2p^4$ 	9 <b>F</b> $1s^2 2s^2 2p^5$ 	10 <b>Ne</b> $1s^2 2s^2 2p^6$ 	



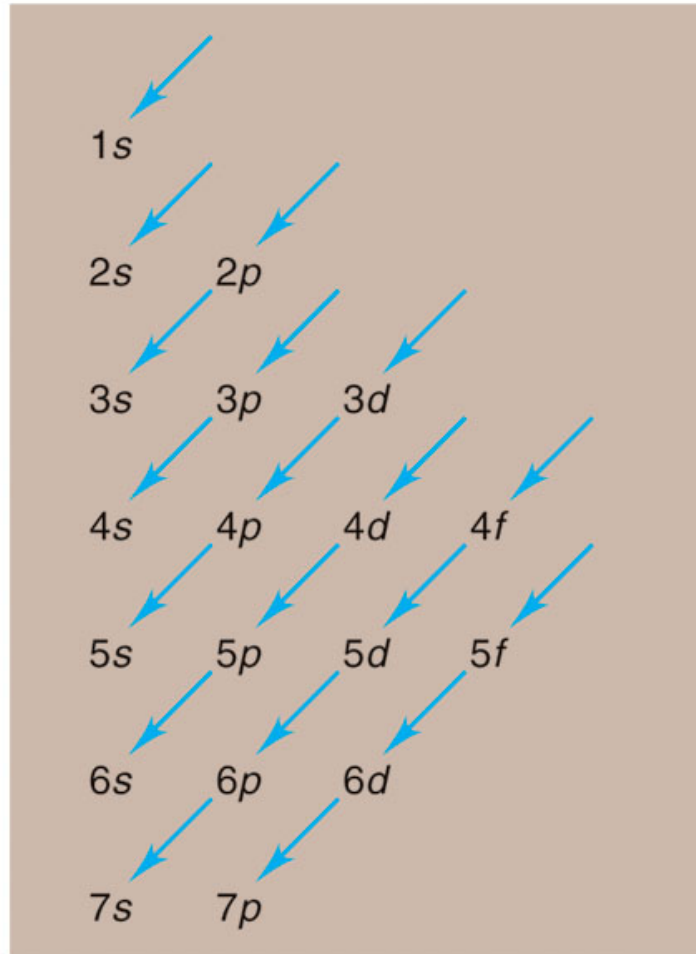
# Silberberg figure 8.6

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# Silberberg figure 8.13

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# Zumdahl figure 12.29

Period number, highest occupied electron level	Representative Elements		<i>d</i> -Transition Elements										Representative Elements					Noble Gases
	1A <i>ns</i> <sup>1</sup>	2A <i>ns</i> <sup>2</sup>											3A <i>ns</i> <sup>2</sup> <i>np</i> <sup>1</sup>	4A <i>ns</i> <sup>2</sup> <i>np</i> <sup>2</sup>	5A <i>ns</i> <sup>2</sup> <i>np</i> <sup>3</sup>	6A <i>ns</i> <sup>2</sup> <i>np</i> <sup>4</sup>	7A <i>ns</i> <sup>2</sup> <i>np</i> <sup>5</sup>	8A <i>ns</i> <sup>2</sup> <i>np</i> <sup>6</sup>
1	1 H <i>1s</i> <sup>1</sup>	2 He <i>1s</i> <sup>2</sup>																
2	3 Li <i>2s</i> <sup>1</sup>	4 Be <i>2s</i> <sup>2</sup>											5 B <i>2s</i> <sup>2</sup> <i>2p</i> <sup>1</sup>	6 C <i>2s</i> <sup>2</sup> <i>2p</i> <sup>2</sup>	7 N <i>2s</i> <sup>2</sup> <i>2p</i> <sup>3</sup>	8 O <i>2s</i> <sup>2</sup> <i>2p</i> <sup>4</sup>	9 F <i>2s</i> <sup>2</sup> <i>2p</i> <sup>5</sup>	10 Ne <i>2s</i> <sup>2</sup> <i>2p</i> <sup>6</sup>
3	11 Na <i>3s</i> <sup>1</sup>	12 Mg <i>3s</i> <sup>2</sup>											13 Al <i>3s</i> <sup>2</sup> <i>3p</i> <sup>1</sup>	14 Si <i>3s</i> <sup>2</sup> <i>3p</i> <sup>2</sup>	15 P <i>3s</i> <sup>2</sup> <i>3p</i> <sup>3</sup>	16 S <i>3s</i> <sup>2</sup> <i>3p</i> <sup>4</sup>	17 Cl <i>3s</i> <sup>2</sup> <i>3p</i> <sup>5</sup>	18 Ar <i>3s</i> <sup>2</sup> <i>3p</i> <sup>6</sup>
4	19 K <i>4s</i> <sup>1</sup>	20 Ca <i>4s</i> <sup>2</sup>	21 Sc <i>4s</i> <sup>2</sup> <i>3d</i> <sup>1</sup>	22 Ti <i>4s</i> <sup>2</sup> <i>3d</i> <sup>2</sup>	23 V <i>4s</i> <sup>2</sup> <i>3d</i> <sup>3</sup>	24 Cr <i>4s</i> <sup>1</sup> <i>3d</i> <sup>5</sup>	25 Mn <i>4s</i> <sup>2</sup> <i>3d</i> <sup>5</sup>	26 Fe <i>4s</i> <sup>2</sup> <i>3d</i> <sup>6</sup>	27 Co <i>4s</i> <sup>1</sup> <i>3d</i> <sup>7</sup>	28 Ni <i>4s</i> <sup>2</sup> <i>3d</i> <sup>8</sup>	29 Cu <i>4s</i> <sup>1</sup> <i>3d</i> <sup>10</sup>	30 Zn <i>4s</i> <sup>2</sup> <i>3d</i> <sup>10</sup>	31 Ga <i>4s</i> <sup>2</sup> <i>4p</i> <sup>1</sup>	32 Ge <i>4s</i> <sup>2</sup> <i>4p</i> <sup>2</sup>	33 As <i>4s</i> <sup>2</sup> <i>4p</i> <sup>3</sup>	34 Se <i>4s</i> <sup>2</sup> <i>4p</i> <sup>4</sup>	35 Br <i>4s</i> <sup>2</sup> <i>4p</i> <sup>5</sup>	36 Kr <i>4s</i> <sup>2</sup> <i>4p</i> <sup>6</sup>
5	37 Rb <i>5s</i> <sup>1</sup>	38 Sr <i>5s</i> <sup>2</sup>	39 Y <i>5s</i> <sup>2</sup> <i>4d</i> <sup>1</sup>	40 Zr <i>5s</i> <sup>2</sup> <i>4d</i> <sup>2</sup>	41 Nb <i>5s</i> <sup>1</sup> <i>4d</i> <sup>4</sup>	42 Mo <i>5s</i> <sup>1</sup> <i>4d</i> <sup>5</sup>	43 Tc <i>5s</i> <sup>1</sup> <i>4d</i> <sup>6</sup>	44 Ru <i>5s</i> <sup>1</sup> <i>4d</i> <sup>7</sup>	45 Rh <i>5s</i> <sup>1</sup> <i>4d</i> <sup>8</sup>	46 Pd <i>4d</i> <sup>10</sup>	47 Ag <i>5s</i> <sup>1</sup> <i>4d</i> <sup>10</sup>	48 Cd <i>5s</i> <sup>2</sup> <i>4d</i> <sup>10</sup>	49 In <i>5s</i> <sup>2</sup> <i>5p</i> <sup>1</sup>	50 Sn <i>5s</i> <sup>2</sup> <i>5p</i> <sup>2</sup>	51 Sb <i>5s</i> <sup>2</sup> <i>5p</i> <sup>3</sup>	52 Te <i>5s</i> <sup>2</sup> <i>5p</i> <sup>4</sup>	53 I <i>5s</i> <sup>2</sup> <i>5p</i> <sup>5</sup>	54 Xe <i>5s</i> <sup>2</sup> <i>5p</i> <sup>6</sup>
6	55 Cs <i>6s</i> <sup>1</sup>	56 Ba <i>6s</i> <sup>2</sup>	57 La* <i>6s</i> <sup>2</sup> <i>5d</i> <sup>1</sup>	72 Hf <i>5f</i> <sup>14</sup> <i>6s</i> <sup>2</sup> <i>5d</i> <sup>2</sup>	73 Ta <i>6s</i> <sup>2</sup> <i>5d</i> <sup>3</sup>	74 W <i>6s</i> <sup>2</sup> <i>5d</i> <sup>4</sup>	75 Re <i>6s</i> <sup>2</sup> <i>5d</i> <sup>5</sup>	76 Os <i>6s</i> <sup>2</sup> <i>5d</i> <sup>6</sup>	77 Ir <i>6s</i> <sup>1</sup> <i>5d</i> <sup>7</sup>	78 Pt <i>6s</i> <sup>1</sup> <i>5d</i> <sup>9</sup>	79 Au <i>6s</i> <sup>1</sup> <i>5d</i> <sup>10</sup>	80 Hg <i>6s</i> <sup>2</sup> <i>5d</i> <sup>10</sup>	81 Tl <i>6s</i> <sup>2</sup> <i>6p</i> <sup>1</sup>	82 Pb <i>6s</i> <sup>2</sup> <i>6p</i> <sup>2</sup>	83 Bi <i>6s</i> <sup>2</sup> <i>6p</i> <sup>3</sup>	84 Po <i>6s</i> <sup>2</sup> <i>6p</i> <sup>4</sup>	85 At <i>6s</i> <sup>2</sup> <i>6p</i> <sup>5</sup>	86 Rn <i>6s</i> <sup>2</sup> <i>6p</i> <sup>6</sup>
7	87 Fr <i>7s</i> <sup>1</sup>	88 Ra <i>7s</i> <sup>2</sup>	89 Ac** <i>7s</i> <sup>2</sup> <i>6d</i> <sup>1</sup>	104 Rf <i>7s</i> <sup>2</sup> <i>6d</i> <sup>2</sup>	105 Db <i>7s</i> <sup>2</sup> <i>6d</i> <sup>3</sup>	106 Sg <i>7s</i> <sup>2</sup> <i>6d</i> <sup>4</sup>	107 Bh <i>7s</i> <sup>2</sup> <i>6d</i> <sup>5</sup>	108 Hs <i>7s</i> <sup>2</sup> <i>6d</i> <sup>6</sup>	109 Mt <i>7s</i> <sup>2</sup> <i>6d</i> <sup>7</sup>	110 Ds <i>7s</i> <sup>2</sup> <i>6d</i> <sup>8</sup>	111 Uuu <i>7s</i> <sup>1</sup> <i>6d</i> <sup>10</sup>	112 Uub <i>7s</i> <sup>2</sup> <i>6d</i> <sup>10</sup>		114 Uuq <i>7s</i> <sup>2</sup> <i>7p</i> <sup>2</sup>				

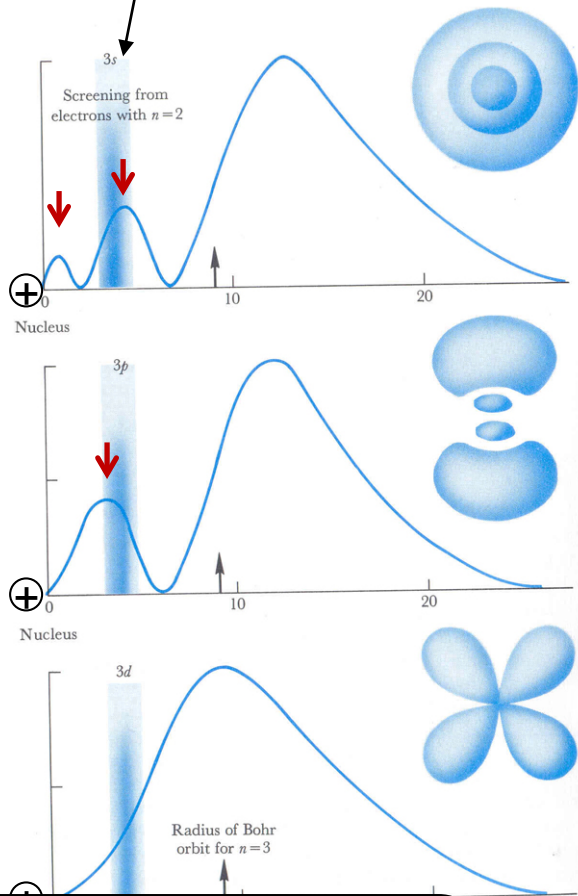
<i>f</i> -Transition Elements														
*Lanthanides	58 Ce <i>6s</i> <sup>2</sup> <i>4f</i> <sup>1</sup> <i>5d</i> <sup>1</sup>	59 Pr <i>6s</i> <sup>2</sup> <i>4f</i> <sup>3</sup> <i>5d</i> <sup>0</sup>	60 Nd <i>6s</i> <sup>2</sup> <i>4f</i> <sup>4</sup> <i>5d</i> <sup>0</sup>	61 Pm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>5</sup> <i>5d</i> <sup>0</sup>	62 Sm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>6</sup> <i>5d</i> <sup>0</sup>	63 Eu <i>6s</i> <sup>2</sup> <i>4f</i> <sup>7</sup> <i>5d</i> <sup>0</sup>	64 Gd <i>6s</i> <sup>2</sup> <i>4f</i> <sup>7</sup> <i>5d</i> <sup>1</sup>	65 Tb <i>6s</i> <sup>2</sup> <i>4f</i> <sup>9</sup> <i>5d</i> <sup>0</sup>	66 Dy <i>6s</i> <sup>2</sup> <i>4f</i> <sup>10</sup> <i>5d</i> <sup>0</sup>	67 Ho <i>6s</i> <sup>2</sup> <i>4f</i> <sup>11</sup> <i>5d</i> <sup>0</sup>	68 Er <i>6s</i> <sup>2</sup> <i>4f</i> <sup>12</sup> <i>5d</i> <sup>0</sup>	69 Tm <i>6s</i> <sup>2</sup> <i>4f</i> <sup>13</sup> <i>5d</i> <sup>0</sup>	70 Yb <i>6s</i> <sup>2</sup> <i>4f</i> <sup>14</sup> <i>5d</i> <sup>0</sup>	71 Lu <i>6s</i> <sup>2</sup> <i>4f</i> <sup>14</sup> <i>5d</i> <sup>1</sup>
**Actinides	90 Th <i>7s</i> <sup>2</sup> <i>5f</i> <sup>0</sup> <i>6d</i> <sup>2</sup>	91 Pa <i>7s</i> <sup>2</sup> <i>5f</i> <sup>2</sup> <i>6d</i> <sup>1</sup>	92 U <i>7s</i> <sup>2</sup> <i>5f</i> <sup>3</sup> <i>6d</i> <sup>1</sup>	93 Np <i>7s</i> <sup>2</sup> <i>5f</i> <sup>4</sup> <i>6d</i> <sup>1</sup>	94 Pu <i>7s</i> <sup>2</sup> <i>5f</i> <sup>6</sup> <i>6d</i> <sup>1</sup>	95 Am <i>7s</i> <sup>2</sup> <i>5f</i> <sup>7</sup> <i>6d</i> <sup>1</sup>	96 Cm <i>7s</i> <sup>2</sup> <i>5f</i> <sup>7</sup> <i>6d</i> <sup>1</sup>	97 Bk <i>7s</i> <sup>2</sup> <i>5f</i> <sup>9</sup> <i>6d</i> <sup>1</sup>	98 Cf <i>7s</i> <sup>2</sup> <i>5f</i> <sup>10</sup> <i>6d</i> <sup>1</sup>	99 Es <i>7s</i> <sup>2</sup> <i>5f</i> <sup>11</sup> <i>6d</i> <sup>1</sup>	100 Fm <i>7s</i> <sup>2</sup> <i>5f</i> <sup>12</sup> <i>6d</i> <sup>1</sup>	101 Md <i>7s</i> <sup>2</sup> <i>5f</i> <sup>13</sup> <i>6d</i> <sup>1</sup>	102 No <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>1</sup>	103 Lr <i>7s</i> <sup>2</sup> <i>5f</i> <sup>14</sup> <i>6d</i> <sup>1</sup>

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

**screening by  $n=2$  electrons**



less penetration  
smaller  $Z_{\text{eff}}$   
higher energy

**3s:** 2 radial nodes  
2 “inner electron density maxima”

**3p:** 1 radial node  
1 “inner maxima”

**3d:** 0 radial nodes  
0 “inner maxima”

more penetration  
larger  $Z_{\text{eff}}$   
lower Energy

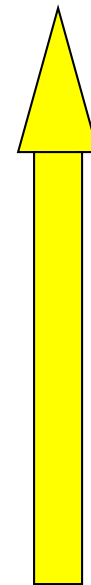
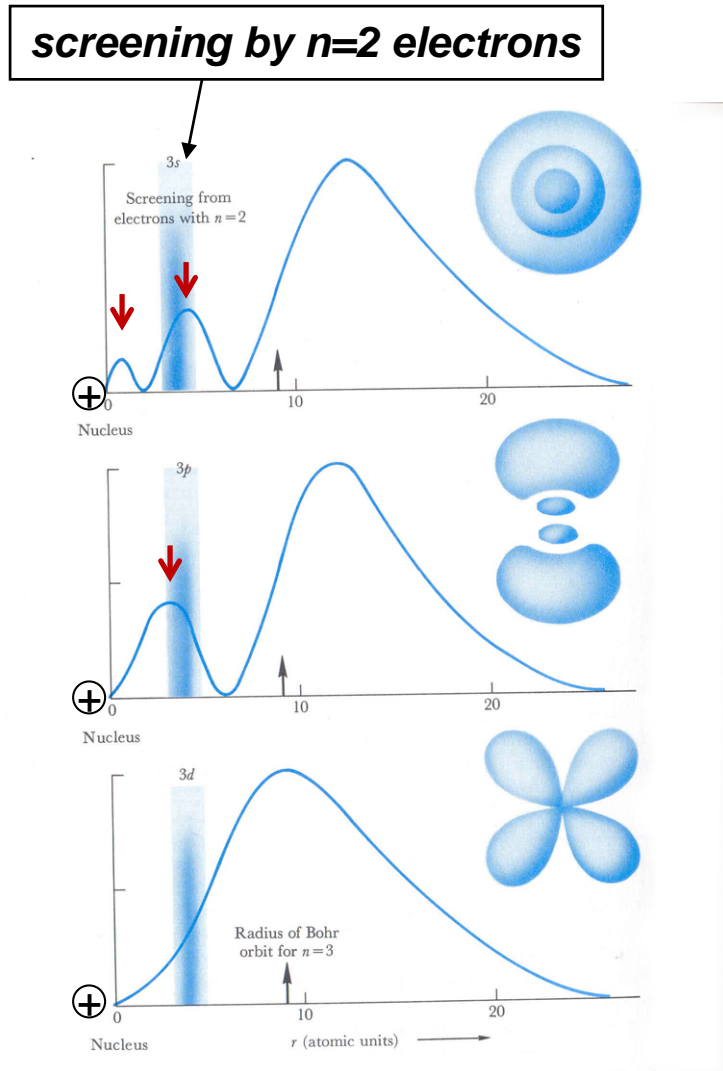


Figure HO 8.6: penetration of 3s vs 3p vs 3d; **radial nodes =  $n - \ell - 1$**



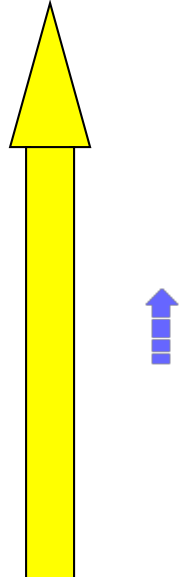
**3s:** 2 radial nodes  
2 "inner electron"

more penetration  
larger  $Z_{\text{eff}}$   
lower Energy

**3p:** 1 radial node  
1 "inner maxima"

**3d:** 0 radial nodes  
0 "inner maxima"

less penetration  
smaller  $Z_{\text{eff}}$   
higher energy



# Why B [He] 2s<sup>2</sup> 2p<sup>1</sup> is 'unambiguous' ground state configuration

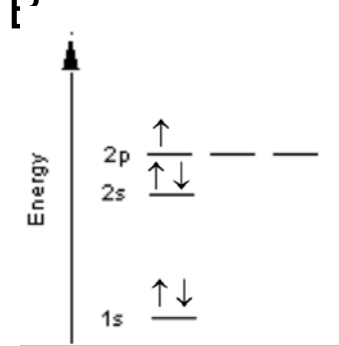
## Experimental spectrum (states) of B

ASD DATA INFORMATION  
 LINES LEVELS List of Spectra Ground States & Ionization Energies Bibliography Help

### NIST Atomic Spectra Database Levels Data

B I 125 Levels Found  
 Z = 5, B isoelectronic sequence

Example of how to reference these results  
 Kramida, A., Ralchenko, Yu., Reader, J., and Spectra Database (ver. 5.0), [Online]. Available October 17]. National Institute of Standards & Technology



ground state of boron: 5 e<sup>-</sup>

configuration: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>1</sup>

Some data for neutral and singly-charged ions are available in the [Handbook of Basic Atomic Spectroscopic Data](#)

Configuration	Term	J	Level (cm <sup>-1</sup> )
2s <sup>2</sup> 2p	2P°	1/2	0.0000
		3/2	15.287
2s2p <sup>2</sup>	4P	1/2	28 647.43+x
		3/2	28 652.07+x
		5/2	28 658.40+x
2s <sup>2</sup> 3s	2S	1/2	40 039.6907
2s2p <sup>2</sup>	2D	5/2	47 856.809
		3/2	47 857.125
2s <sup>2</sup> 3p	2P°	1/2	48 611.8663

Only 'one' energy state  
 (ignore 3/2 vs 1/2)





# Why B [He] 2s<sup>2</sup> 2p<sup>1</sup> is *'unambiguous'* ground state configuration

## Experimental spectrum (states) of B

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		3/2	28 652.07+x
		5/2	28 658.40+x
2s <sup>2</sup> 3s	2S	1/2	40 039.6907
2s2p <sup>2</sup>	2D	5/2	47 856.809
		3/2	47 857.125
2s <sup>2</sup> 3p	2P°	1/2	48 611.8663

Only 'one' energy state  
 (ignore 3/2 vs 1/2)

Excited states have excited  
 [He] 2s<sup>1</sup> 2p<sup>2</sup> configuration



# Why C [He] 2s<sup>2</sup> 2p<sup>2</sup> is 'ambiguous' ground state configuration

## Experimental spectrum (states) of C

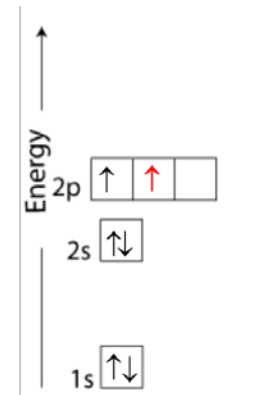
**ASD** DATA INFORMATION  
 LINES LEVELS List of Spectra Ground States & Ionization Energies Bibliogr.

### NIST Atomic Spectra Database Levels Data

C I 282 Levels Found  
 Z = 6, C isoelectronic sequence

Example of how to reference:  
 Kramida, A., Ralchenko, Yu.,  
 Spectra Database (ver. 5.0), [October 17]. National Institute

Some data for neutral and singly-charged ions are available in the [Handbook of Basic Atomic Spectroscopy](#)



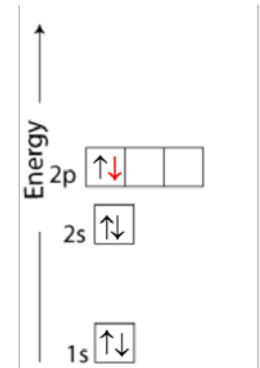
lowest energy: ground state

Configuration	Term	J	Level (cm <sup>-1</sup> )
---------------	------	---	---------------------------

2s <sup>2</sup> 2p <sup>2</sup>	<sup>3</sup> P	0	0.00
		1	16.40
		2	43.40
2s <sup>2</sup> 2p <sup>2</sup>	<sup>1</sup> D	2	10 192.63
2s <sup>2</sup> 2p <sup>2</sup>	<sup>1</sup> S	0	21 648.01
2s2p <sup>3</sup>	<sup>5</sup> S <sup>o</sup>	2	33 735.20
2s <sup>2</sup> 2p3s	<sup>3</sup> P <sup>o</sup>	0	60 333.43
		1	60 352.63
		2	60 393.14

Ground energy state  
 (ignore 0 vs 1 vs 2)

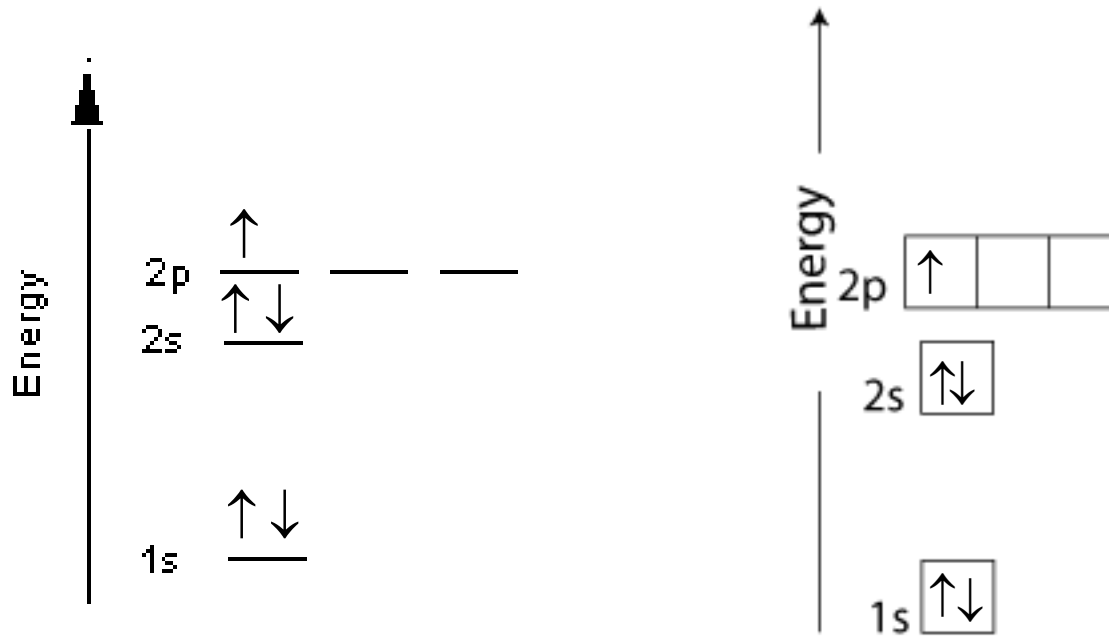
Excited states with same [He] 2s<sup>2</sup> 2p<sup>2</sup> configuration



higher energy: excited state



## *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  $[\text{He}] 2s^2 2p^1$



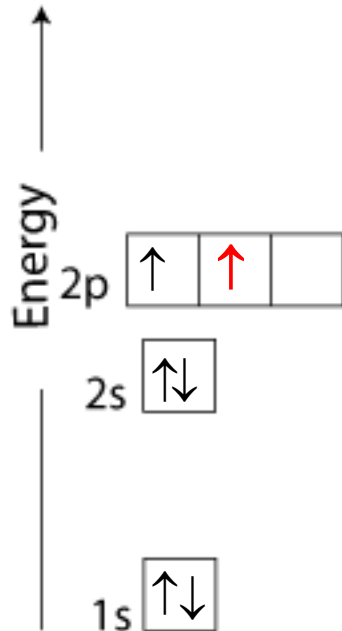
# Hund's Rule



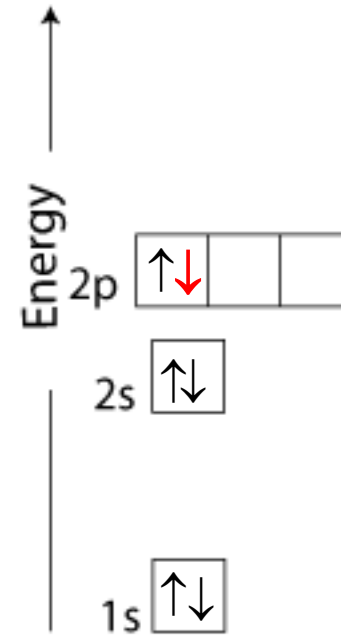
**Friedrich Hund**

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  $[\text{He}] 2s^2 2p^2$



*lowest energy: ground state*



*higher energy: excited state*



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

---

$$E_n \approx - (2.18 \times 10^{-18} \text{ J}) \frac{Z_{\text{eff}}^2}{n^2}$$

smaller  $n \Rightarrow$  lower (more negative) energy  
larger  $Z_{\text{eff}} \Rightarrow$  lower (more negative) energy

who wins for lower energy?

3d vs 4s

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

$Z_{\text{eff}}$ : smaller vs larger **4s wins for lower energy**

0 radial nodes vs 3 radial nodes

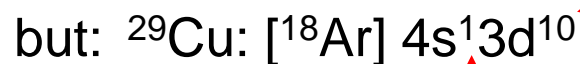
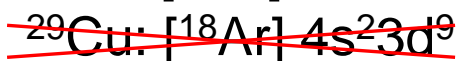
**and the energy winner is :**

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



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:



filled

half-filled

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

