

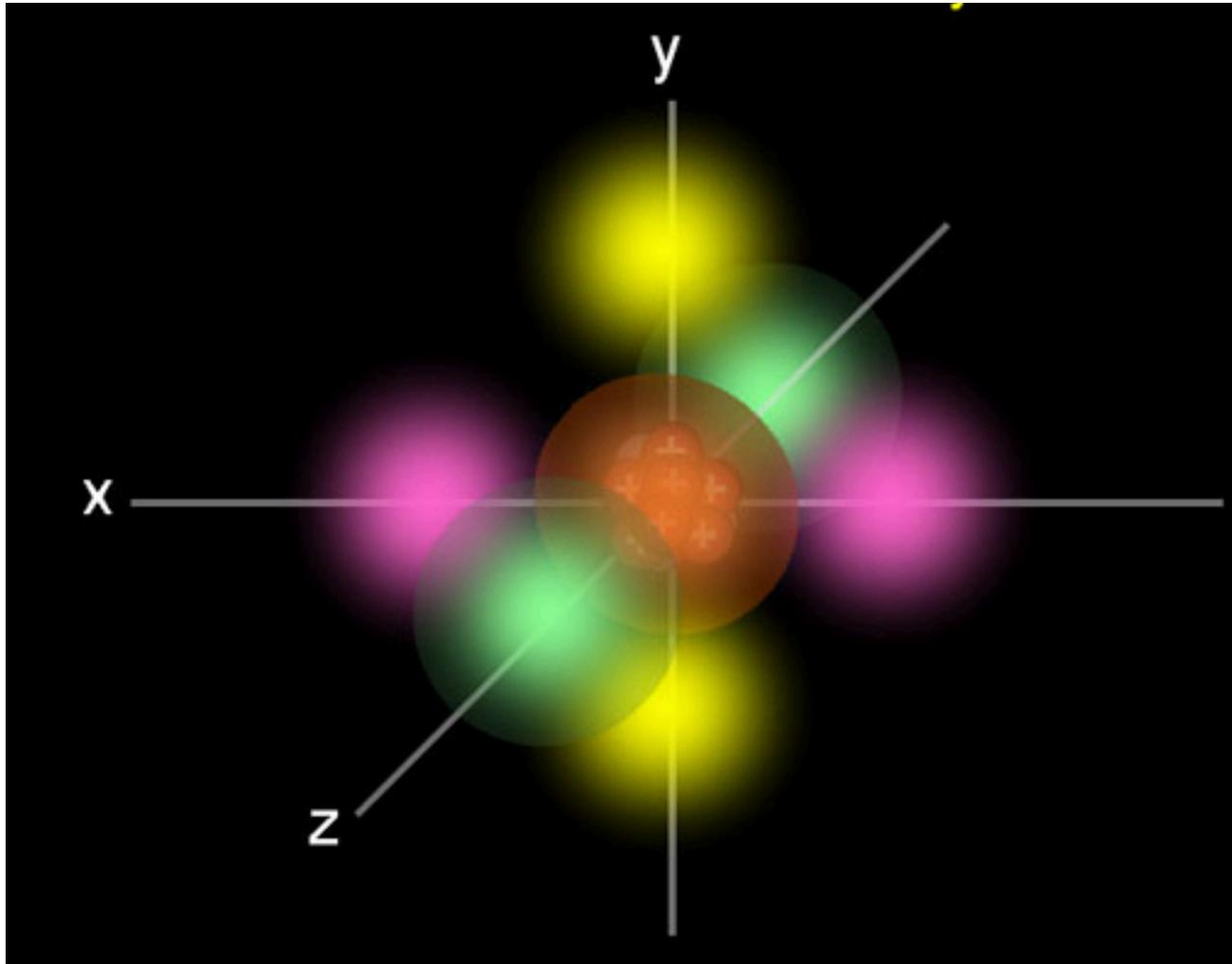
Modern Physics (Phys. IV): 2704

Professor Jasper Halekas
Van Allen 70
MWF 12:30-1:20 Lecture

Announcements

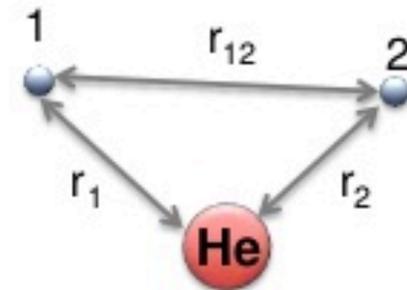
- HW #9 Due Friday
- Lab Q7 (Electron Spin Resonance) this week

Multi-Electron Atoms



Schrödinger Equation for Multi-Electron Atoms

Once we have two or more electrons, the Schrodinger equation **cannot** be solved exactly: *fundamental challenge for quantum chemistry!*



fixed nucleus at origin

Helium atom hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

electron
kinetic energy

electron-nuclear
coulombic attraction

electron
repulsion

Pauli Exclusion Principle

Electrons in an atom are arranged in individual “orbitals” each having a set of quantum numbers (n, l, m_l, m_s)

No two occupied electron orbitals can have the same set of quantum numbers.

State	Principal quantum number n	Orbital quantum number	Magnetic quantum number	Spin quantum number	Maximum number of electrons
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2p	2	1	-1,0,+1	$+\frac{1}{2}, -\frac{1}{2}$	6
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
3p	3	1	-1,0,+1	$+\frac{1}{2}, -\frac{1}{2}$	6
3d	3	2	-2,-1,0,1,2	$+\frac{1}{2}, -\frac{1}{2}$	10

} 8
 } 18

Shell name	Subshell name	Subshell max electrons	Shell max electrons
K	1s	2	2
L	2s	2	2 + 6 = 8
	2p	6	
M	3s	2	2 + 6 + 10 = 18
	3p	6	
	3d	10	

Orbital Filling

Atom	1s	2s	2p			Electronic configuration
Li						$1s^2 2s^1$
Be						$1s^2 2s^2$
B						$1s^2 2s^2 2p^1$
C						$1s^2 2s^2 2p^2$
N						$1s^2 2s^2 2p^3$
O						$1s^2 2s^2 2p^4$
F						$1s^2 2s^2 2p^5$
Ne						$1s^2 2s^2 2p^6$

H	(+1)							
He	(+2)							Filled shell, inert gas
Li	(+3)							Active!
Be	(+4)							
B	(+5)							
C	(+6)							
N	(+7)							
O	(+8)							
F	(+9)							Active!
Ne	(+10)							Stable 2s2p octet, inert gas.
Na	(+11)							Active!
Mg	(+12)							

Periodic Table

Electron Configurations in the Periodic Table

1 H 1s																	2 He 1s
3 Li 2s	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na 3s	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K 4s	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb 5s	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs 6s	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr 7s	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114				
		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

by: Sarah Faizi

Orbital Filling

Atom	1s	2s	2p			Electronic configuration
Li						$1s^2 2s^1$
Be						$1s^2 2s^2$
B						$1s^2 2s^2 2p^1$
C						$1s^2 2s^2 2p^2$
N						$1s^2 2s^2 2p^3$
O						$1s^2 2s^2 2p^4$
F						$1s^2 2s^2 2p^5$
Ne						$1s^2 2s^2 2p^6$

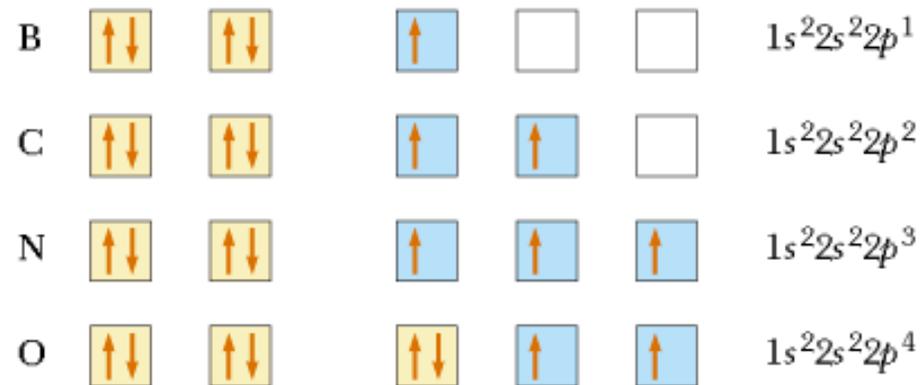
H	(+1)							
He	(+2)							Filled shell, inert gas
Li	(+3)							Active!
Be	(+4)							
B	(+5)							
C	(+6)							
N	(+7)							
O	(+8)							
F	(+9)							Active!
Ne	(+10)							Stable 2s2p octet, inert gas.
Na	(+11)							Active!
Mg	(+12)							

Hund's Rules

- I. The configuration with the highest total spin S has the lowest energy
- II. For a given total spin S , the configuration with the highest total angular momentum L has the lowest energy
- III. For a subshell less (more) than half filled, the configuration with lowest (highest) total angular momentum $J = L + S$ has the lowest energy

Hund's Rule I

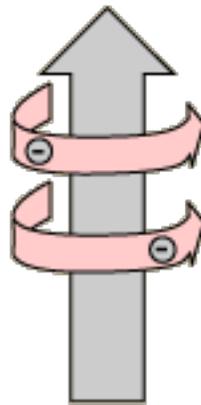
- Electrons in different orbitals are less well screened, so it is energetically favorable to put one electron in every available orbital before putting two in any given orbital



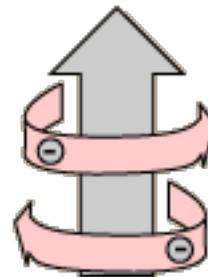
Hund's Rule II

- Semi-classical explanation: If all electrons orbit in a common direction they meet less often and thus have less mutual repulsion

High L, electrons orbiting same direction to add to L value.



Low L, some electrons orbiting in opposite direction to reduce the L value.



Concept Check

- Which set of quantum numbers for two electrons in a 3p subshell is the ground state?

- A. $m_l = 1, m_s = 1/2$ and $m_l = 0, m_s = -1/2$*
- B. $m_l = 1, m_s = 1/2$ and $m_l = -1, m_s = 1/2$*
- C. $m_l = 1, m_s = 1/2$ and $m_l = 0, m_s = 1/2$*
- D. $m_l = 1, m_s = 1/2$ and $m_l = 1, m_s = -1/2$*

Concept Check

- Which set of quantum numbers for two electrons in a 3p subshell is the ground state?

A. $m_l = 1, m_s = 1/2$ and $m_l = 0, m_s = -1/2$

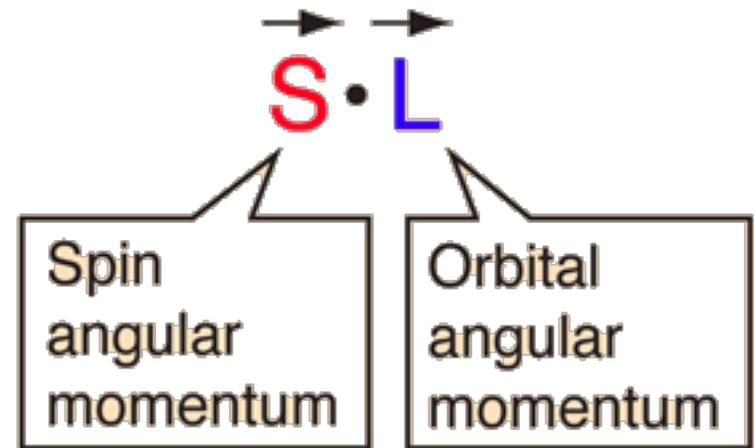
B. $m_l = 1, m_s = 1/2$ and $m_l = -1, m_s = 1/2$

C. $m_l = 1, m_s = 1/2$ and $m_l = 0, m_s = 1/2$

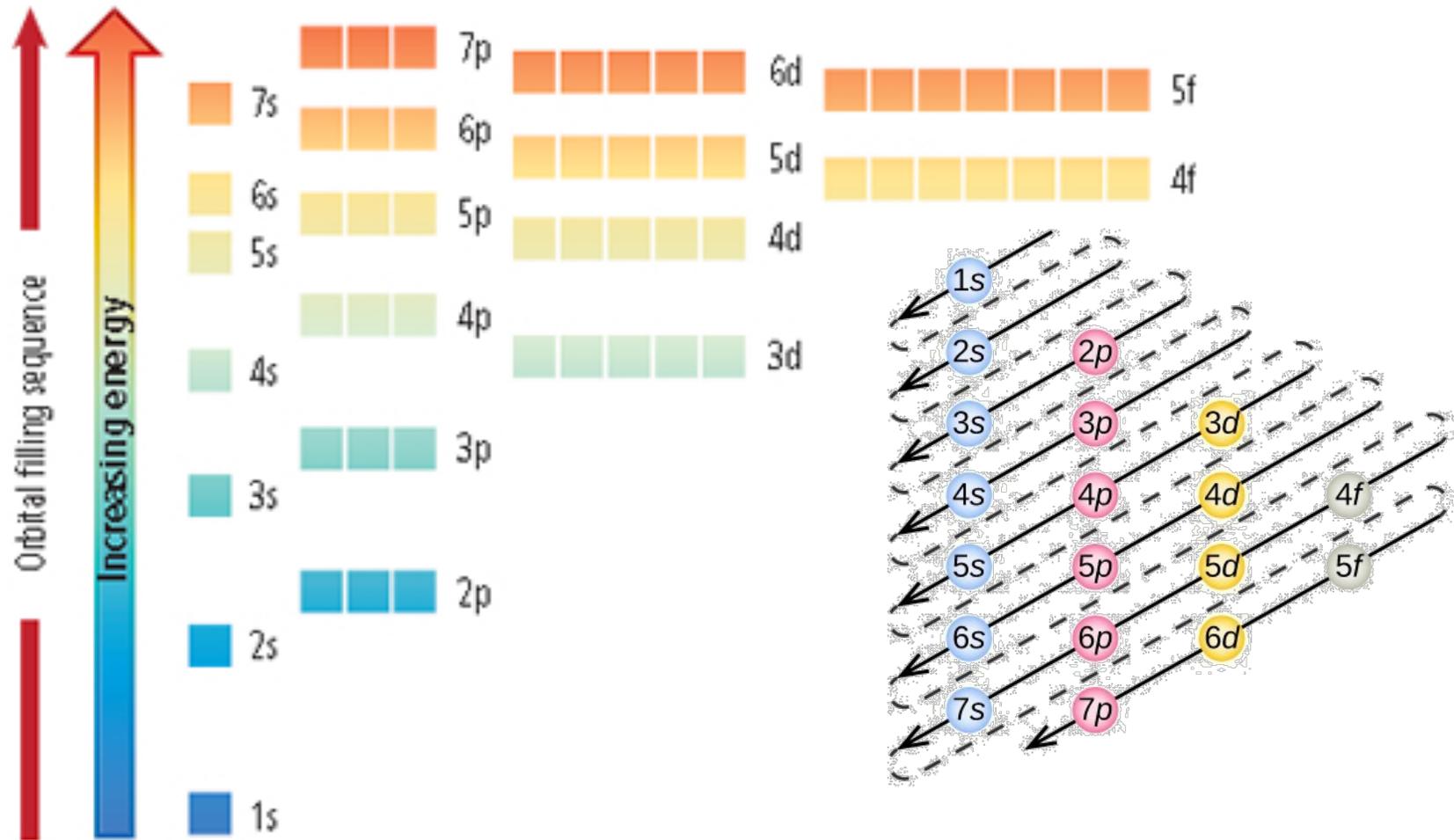
D. $m_l = 1, m_s = 1/2$ and $m_l = 1, m_s = -1/2$

Hund's Rule III

- Spin-Orbit coupling lowers energy levels where L and S are anti-aligned and raises those where they are aligned



Energy Levels



Concept Check

- Lithium has three protons (and four neutrons) in the nucleus, surrounded by three electrons. For the outermost electron (well outside of the inner two), what does the nuclear charge appear to be?
 - 0
 - $\sim +e$
 - $\sim +2e$
 - $\sim +3e$

Concept Check

- Lithium has three protons (and four neutrons) in the nucleus, surrounded by three electrons. For the outermost electron (well outside of the inner two), what does the nuclear charge appear to be?

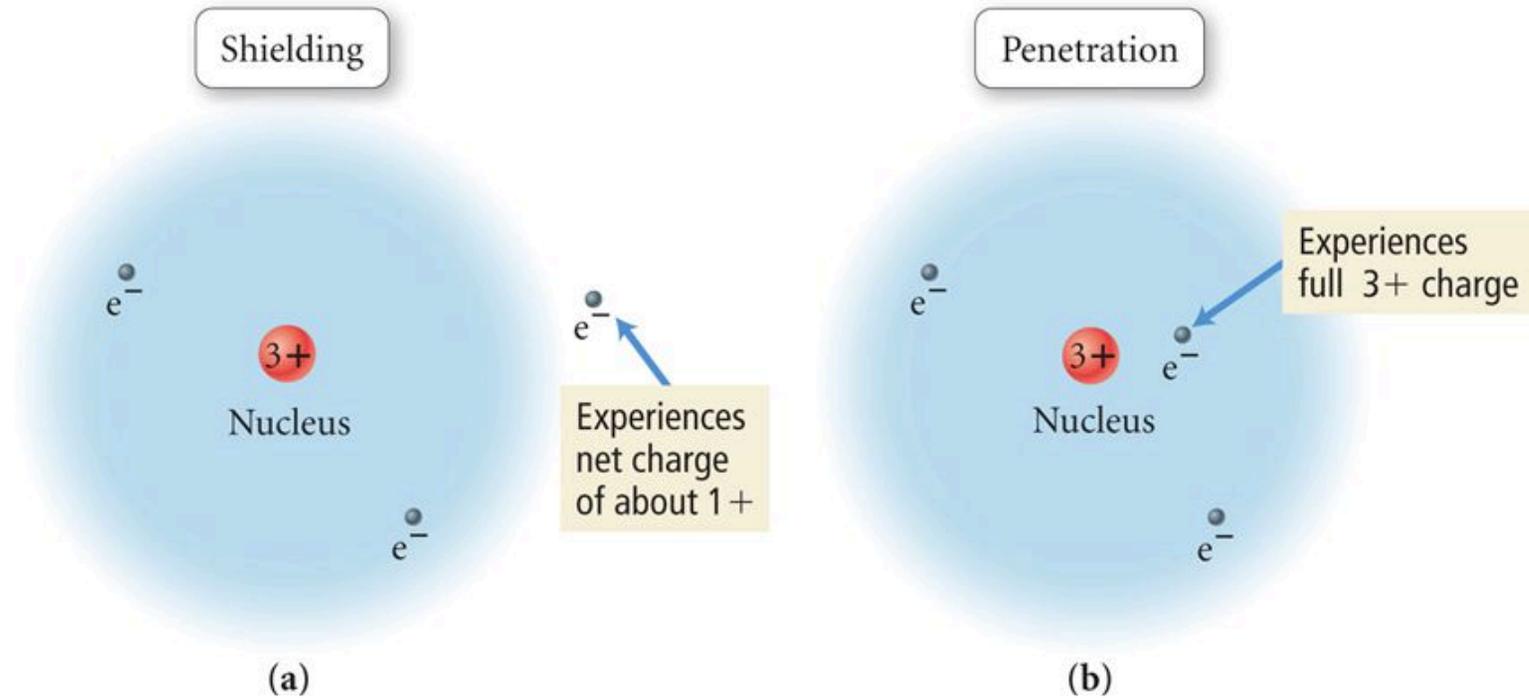
- 0

- $\sim +e$

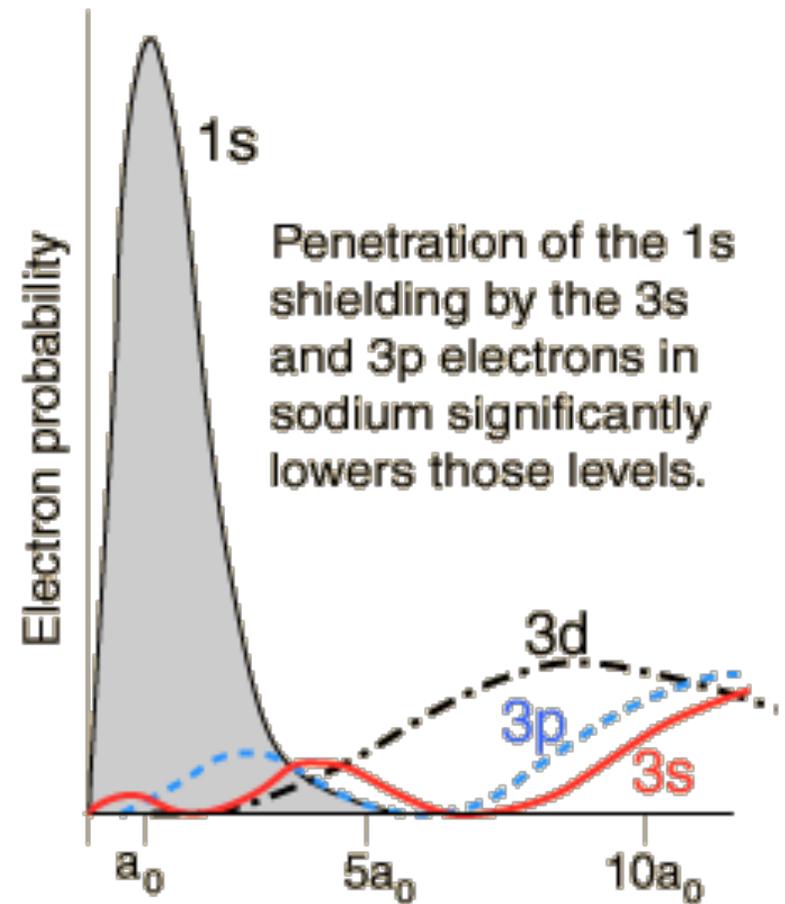
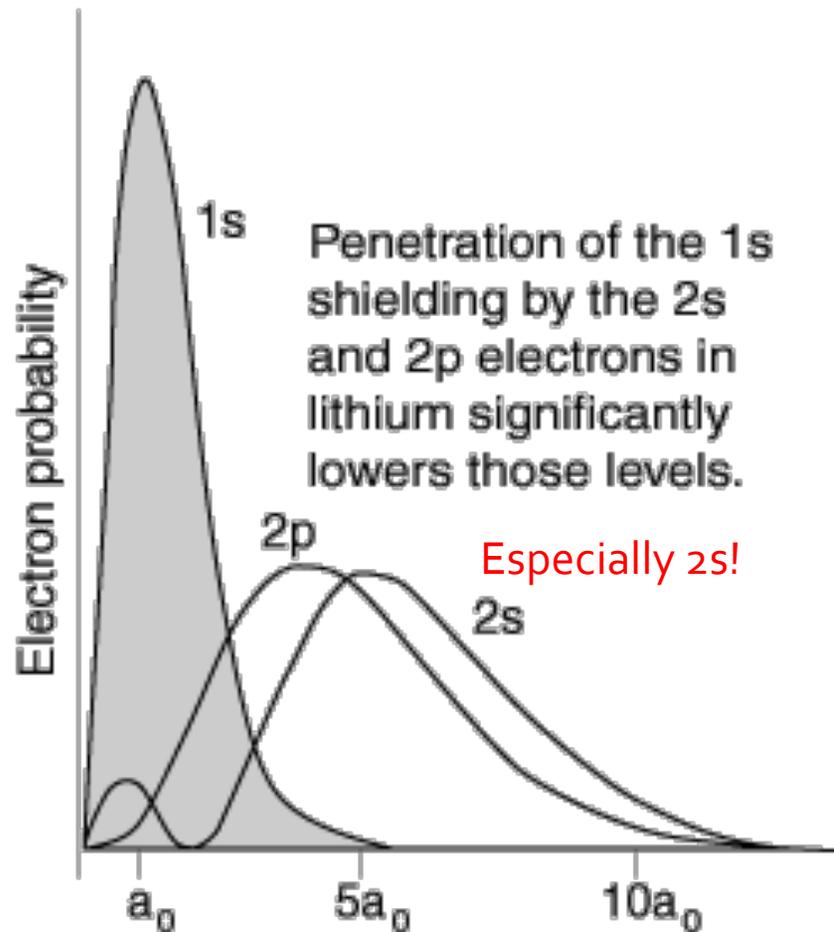
- $\sim +2e$

- $\sim +3e$

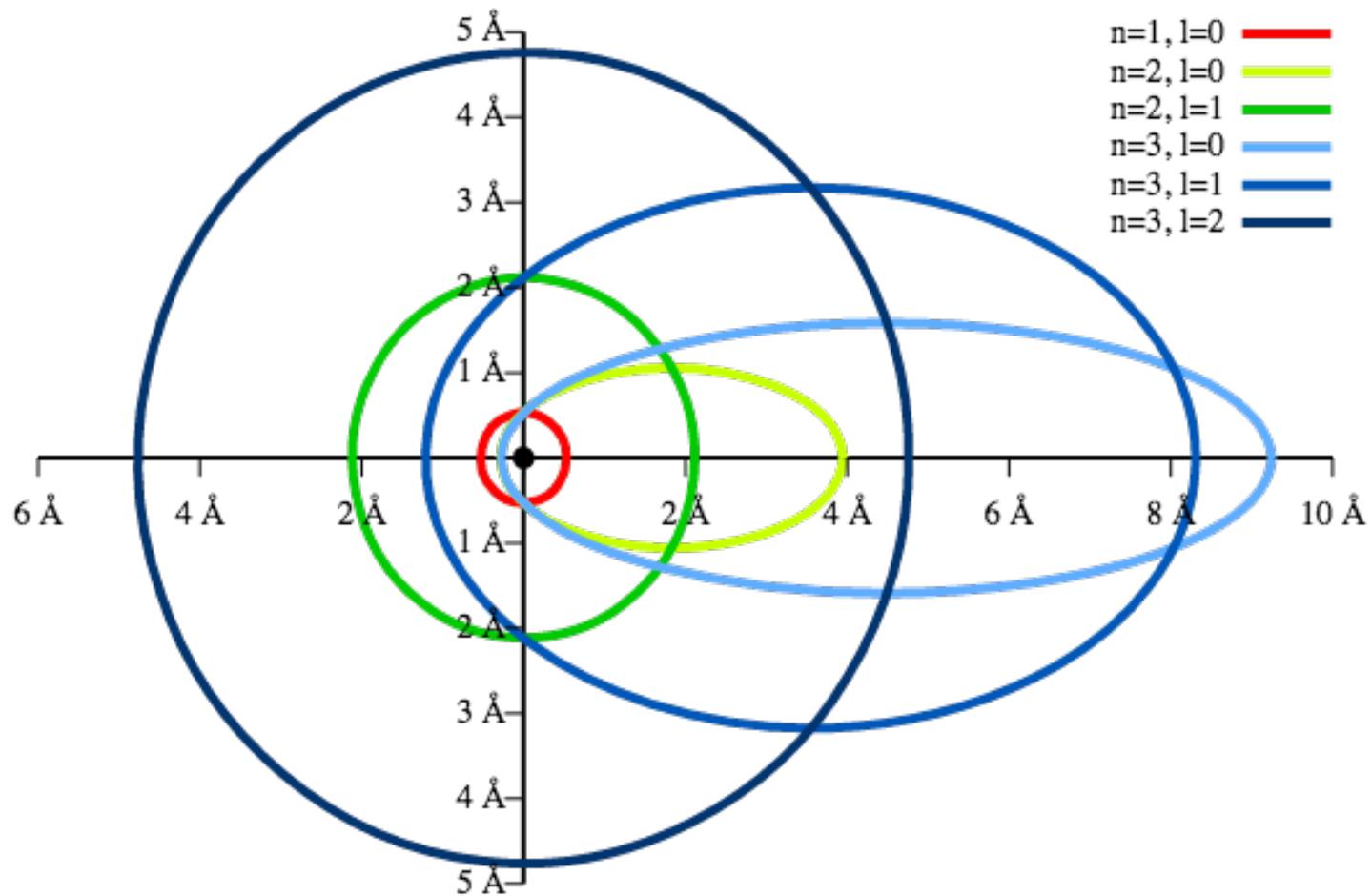
Penetration and Shielding



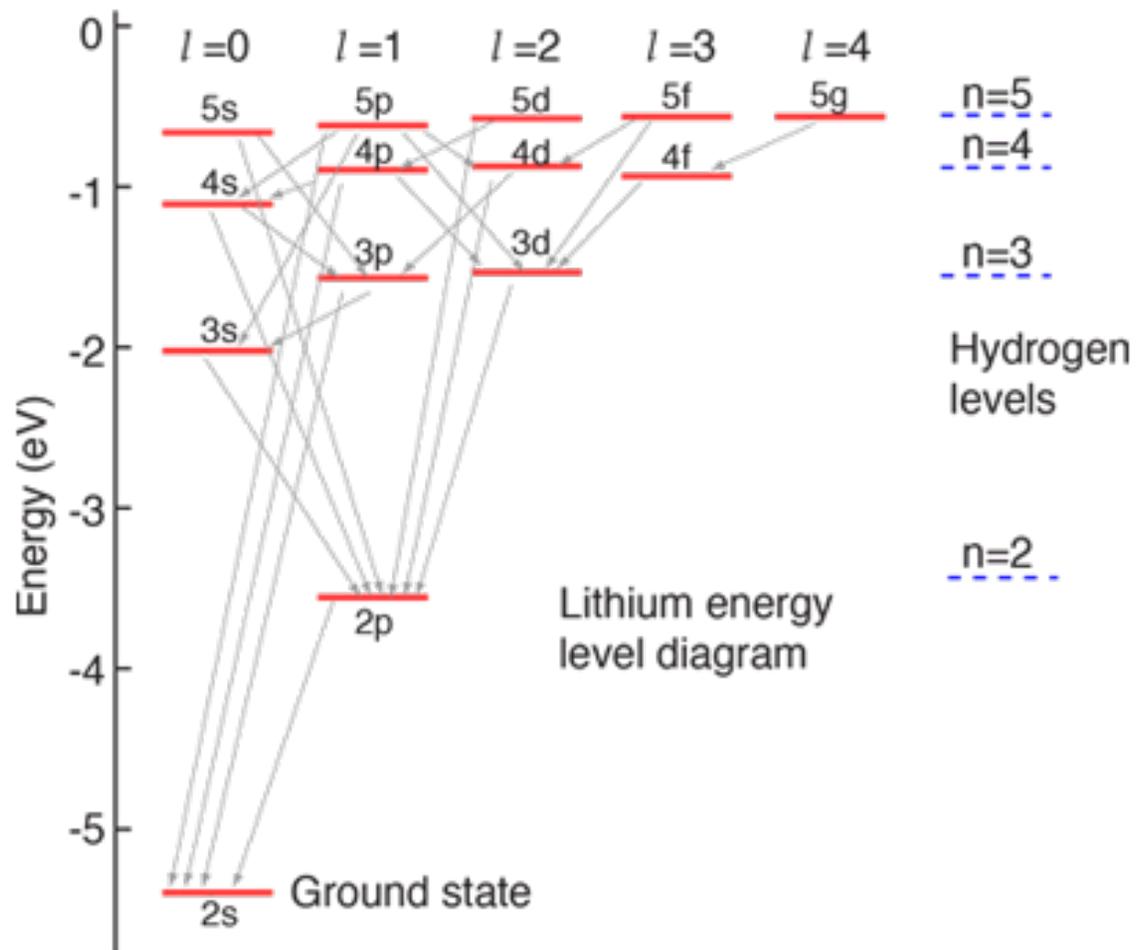
Penetrating Orbits



Penetrating Orbitals



Lithium ($Z=3$) Transitions



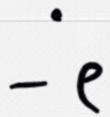
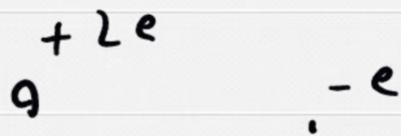
Concept Check

- The binding energy of hydrogen (one electron in $1s$ orbital) is 13.6 eV. Helium has two $1s$ electrons. Would you expect the binding energy of each electron to be...
- Less than for hydrogen?
- Equal to hydrogen?
- Greater than for hydrogen?

Concept Check

- The binding energy of hydrogen (one electron in $1s$ orbital) is 13.6 eV. Helium has two $1s$ electrons. Would you expect the binding energy of each electron to be...
- Less than for hydrogen?
- Equal to hydrogen?
- Greater than for hydrogen?

Helium



E_n for $Z = 2$
w/ no screening

$$E_n = -13.6 \frac{Z^2}{n^2} \\ = -54.4/n^2$$

E_n w/ perfect screening
 $Z_{\text{eff}} = 1 \quad E_n = -13.6/n^2$

Actual $E_1 = -25.4$

Characterize as $E_1 = -13.6 Z_{\text{eff}}^2$

$$\Rightarrow Z_{\text{eff}} \sim 1.37$$

2nd electron screens
 $\sim 31\%$ of nuclear charge

Helium ($Z=2$) Transitions

