Preparing for the Physics GRE: Day 2: Atomic Physics

Daniel T. Citron
dtc65@cornell.edu
3/1/16
http://greprep.dtcitron.com

The Periodic Table

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	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
5	37 Rb	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
6	55 Cs	56 Ba		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
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Lanthanides	57 La	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
Actinides	89 Ac	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

http://en.wikipedia.org/wiki/Periodic_table

The Periodic Table

- A few things worth memorizing:
  - Fact: Z ranges from 1 to (about) 100
  - Noble gases, in order by weight
  - Alkali metals
  - Z for Carbon, Iron (as well as H, He)

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The Hydrogen Atom

- Most complicated system completely solved by quantum: one electron and one proton
- Bohr radius: most probable distance between p and e in hydrogen ground state

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \cong .5 \cdot 10^{-10} m$$

- Allowed energies, where n is the quantum number of the radial state of the atom:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{-13.6eV}{n^2}$$

- It is worth knowing these formulae so you know how they scale as mass or charge is changed (or at least be able to reason them out using dimensional analysis)

Positronium

- Electron-positron bound state
- Mass that appears in H spectrum is *reduced* e-p mass:

$$m_{reduced} = \left(\frac{1}{m_p} + \frac{1}{m_e} \right)^{-1}$$

- Since $m_p >> m_e$, the reduced mass is set to m_e
- But for positronium, what is the new reduced mass?
- How does the energy spectrum change?
- How does the Bohr radius change?

99. The positronium "atom" consists of an electron and a positron bound together by their mutual Coulomb attraction and moving about their center of mass, which is located halfway between them. Thus the positronium "atom" is somewhat analogous to a hydrogen atom. The ground-state binding energy of hydrogen is 13.6 electron volts. What is the ground-state binding energy of positronium?

(A) $\left(\frac{1}{2}\right)^2 \times 13.6$ eV

(B) $\frac{1}{2} \times 13.6$ eV

(C) 13.6 eV

(D) 2×13.6 eV

(E) $(2)^2 \times 13.6$ eV

Spectrum for Hydrogen (and for Higher-Z atoms)

- Photons are emitted when atomic electrons fall from high n to low n states
- Photon energy is equal to the energy difference between the two energy states
- As a first approximation, can treat high-Z atoms as having effective charge Ze

$$\hbar\omega = -13.6eV \cdot Z^2\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_o^{\,2}}\right)$$

9. In the spectrum of hydrogen, what is the ratio of the longest wavelength in the Lyman series ($n_f = 1$) to the longest wavelength in the Balmer series ($n_f = 2$) ?

(A) 5/27
(B) 1/3
(C) 4/9
(D) 3/2
(E) 3

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$$\hbar\omega = -13.6eV \cdot Z^2\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_o^{\,2}}\right)$$

- Long wavelength => small frequency
- n_f and n_0 must be close to one another
- Balmer $n_0 = 3$, $n_f = 2$: -5/36
- Lyman $n_0 = 2$, $n_f = 1$: -3/4
- Take the ratio…

Ionization energy

- How much energy does it take to ionize an atom, so that one (or more) electrons are removed from their orbits completely?
- Think of the energy required as an atomic transition from n_0 to $n_f \rightarrow \infty$:

$$E_{ionization} = \frac{13.6eV \cdot Z^2}{n_o^{\,2}}$$

18. The energy required to remove both electrons from the helium atom in its ground state is 79.0 eV. How much energy is required to ionize helium (i.e., to remove one electron) ?

(A) 24.6 eV
(B) 39.5 eV
(C) 51.8 eV
(D) 54.4 eV
(E) 65.4 eV

Helium Ionization Energy

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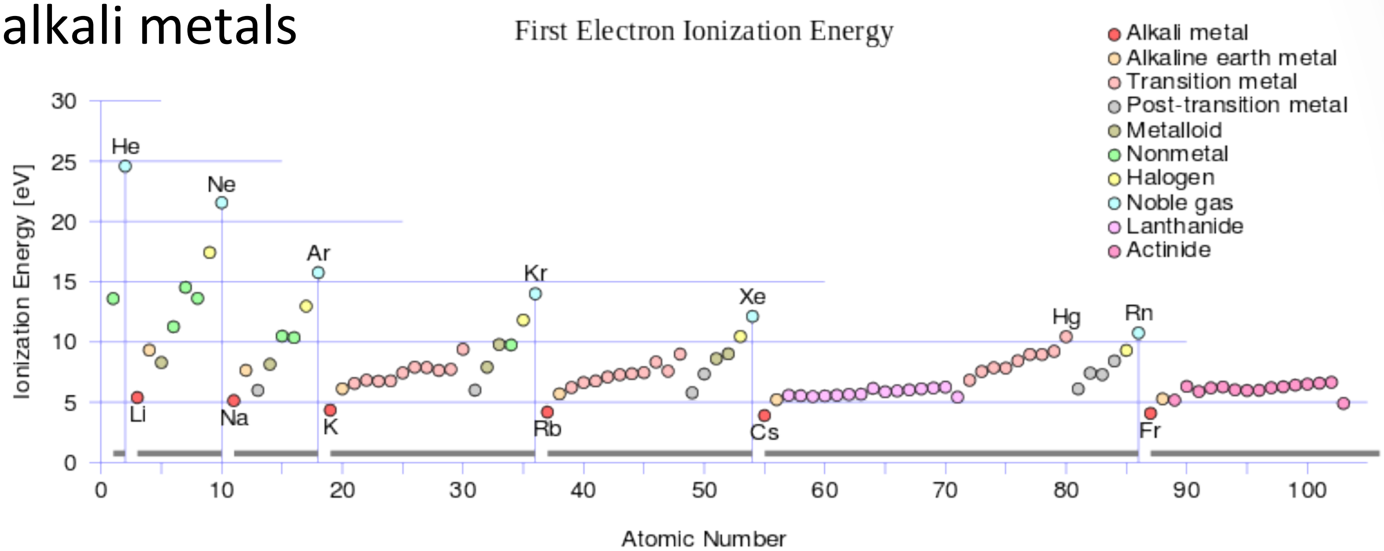
    (D) 54.4 eV
    (E) 65.4 eV

$$E_{ionization} = \frac{13.6eV \cdot Z^2}{n_o^{\,2}}$$

- The energy to remove two He electrons equals the energy required to ionize He (remove the first) plus the energy required to remove the second
- Treat ionized Helium as a hydrogen-like atom with Z = 2
- What is the ionization energy of ionized Helium?
  - 4 * 13.6 eV = 54.4 eV
  - => 79 eV-54.4 eV = 24.6 eV

Ionization energy

- Generally, ionization energy is highest for noble gases, lowest for alkali metals



39. Which of the following atoms has the lowest ionization potential?

(A) ${}^{2}_{4}He$

(B) ${}^{7}_{14}N$

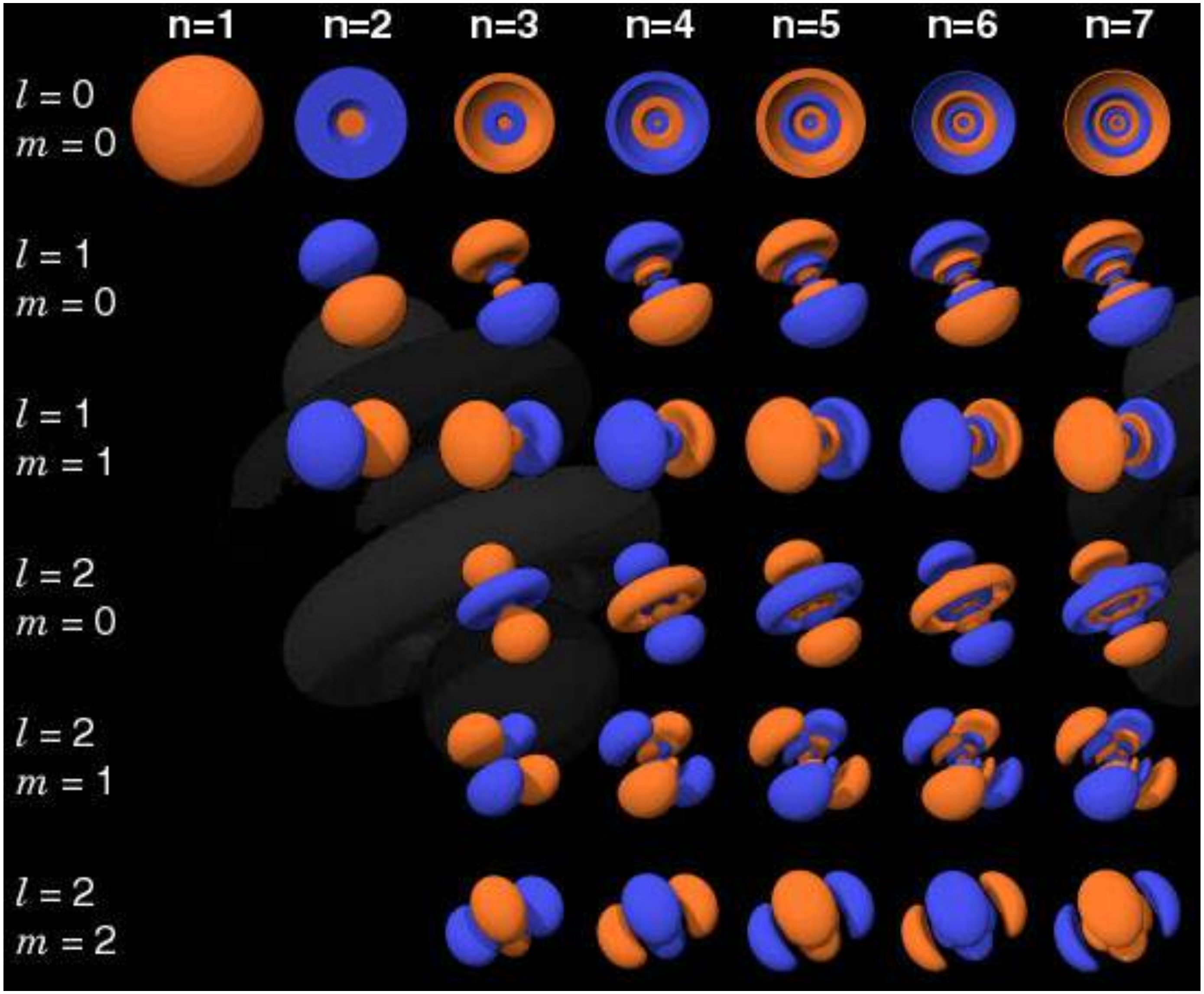
(C) ${}^{8}_{16}O$

(D) ${}^{18}_{40}Ar$

(E) ${}^{55}_{133}Cs$

http://en.wikipedia.org/wiki/Ionization_energy

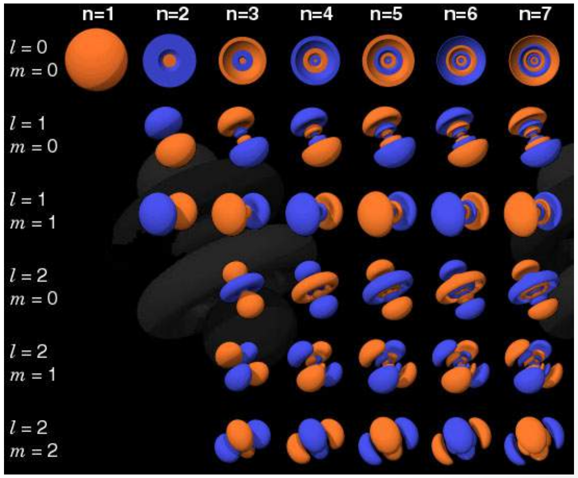
Orbitals



http://chemistry.beloit.edu/Stars/pages/orbitals.html

Orbitals

- Orbitals are denoted by their quantum numbers
- **n** is the **radial** quantum number, determines energy eigenstate
- **l** is the **azimuthal** quantum number: 0, 1, 2, … n-1
- **m is the magnetic** quantum number: -l, -l+1, … l-1, l
  - l > 0 states are 2l+1-fold degenerate
- l, m = 0 states are spherically symmetric: nonzero l, m states have nonzero angular momentum and break symmetry
- For each n, there are n^2 - n possible states to fill
- We distinguish these angular momentum states as follows:
  - s: l = 0 (**s**harp)
  - p: l = 1 (**p**rincipal)
  - d: l = 2 (**d**iffuse)
  - f: l = 3 (**f**undamental)

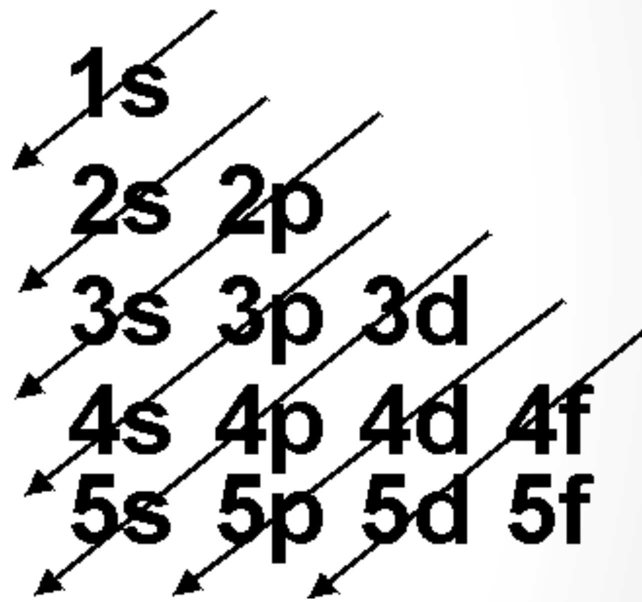


How ground state orbitals are filled

- I have Z electrons in an atomic ground state, which orbitals do they fill?
- Notation: (n, l-state label, number of electrons in state, up to 2)
- Filling is as follows, from left to right:

1s2 2s2 2p6 3s2 3p6 4s2 3d10 …

- (Note, for example, that 4s are filled before 3d)
- After Helium, noble gases occur when p-orbitals are filled:
  - He: 1s2, Ne: 1s2 2s2 2p6,
  - Ar: 1s2 2s2 2p6 3s2 3p6, etc.
- Sometimes this notation is abbreviated:
  - Ca: 1s2 2s2 2p6 3s2 3p6 4s2= Ar 4s2



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- Notation: (n, l-state label, number of electrons in state, up to 2)

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30. The configuration of the potassium atom in its ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. Which of the following statements about potassium is true?

(A) Its $n = 3$ shell is completely filled.

(B) Its $4s$ subshell is completely filled.

(C) Its least tightly bound electron has $\ell = 4$.

(D) Its atomic number is 17.

(E) Its electron charge distribution is spherically symmetrical.

How ground state orbitals are filled

- Notation: (n, l-state label, number of electrons in state, up to 2)

  1s2 2s2 2p6 3s2 3p6 4s2 3d10 4p6

- (A) What about 3d?
- (B) Only 1 electron in 4s
- (C) No l = 4 electrons here
- (D) I count 19 orbitals filled
- (E) s-orbitals have 0 net angular momentum and are spherically symmetric

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6. An atom has filled $n = 1$ and $n = 2$ levels. How many electrons does the atom have?

(A) 2
(B) 4
(C) 6
(D) 8
(E) 10

Spectroscopic notation $^{2S+1}L_J$

- There's yet another notation for the state of atoms, that can also account for states above the ground state
- S is the total spin momentum of the electrons
  - Electrons paired together in the same state have 0 net spin
  - Spin-up and spin-down half-shells are filled separately
  - That is to say, three p states (px, py, pz) are filled as follows: (1,0,0), (1,1,0), (1,1,1), (1,1,2), (1,2,2), (2,2,2)
  - Only unpaired electrons contribute to S
- L is the l-state label of the atom (S, P, D, F, etc)
  - Each half-shell is filled in order: l, l-1, l-2, … 1-l, -l
- J is the total angular momentum, ranging from L+S to |L-S|
  - |L-S| if outermost subshell is only half filled
  - L+S if outermost subshell is completely filled

Spectroscopic notation $^{2S+1}L_J$

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  - |L-S| if outermost subshell is only half filled
  - L+S if outermost subshell is completely filled
- Examples:
- Mg: 1s2 2s2 2p6 3s2 -> s = 0, l = 0, j = 0 => $^{1}S_{0}$
  - Example of an atom with all shells filled
- C: He 2p2 -> s = 1, l = 1 + 0, j = l-s = 0 => $^{1}P_{0}$
- F: He 2p5 -> s = ½, l = 1+0-1+1+0 = 1, j = l+s = 3/2 => $^{2}P_{3/2}$
- P: Ne 3s2 3p3 -> s = 3/2, l = 1+0-1= 0, j = l-s = 3/2 => $^{4}S_{3/2}$

Spectroscopic notation $^{2S+1}L_J$

- Two examples:

76. The configuration of three electrons ls2p3p has which of the following as the value of its maximum possible total angular momentum quantum number?

(A) $\frac{7}{2}$

(B) 3

(C) $\frac{5}{2}$

(D) 2

(E) $\frac{3}{2}$

84. Sodium has eleven electrons and the sequence in which energy levels fill in atoms is $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, etc. What is the ground state of sodium in the usual notation $^{2S+1}L_J$?

(A) $^1S_0$ (B) $^2S_{\frac{1}{2}}$ (C) $^1P_0$

(D) $^2P_{\frac{1}{2}}$ (E) $^3P_{\frac{1}{2}}$

Spectroscopic notation $^{2S+1}L_J$

- Two examples:
- Note the atom is out of its ground state
  - S = 3/2
  - l = 0+1+1 = 2

76. The configuration of three electrons ls2p3p has which of the following as the value of its maximum possible total angular momentum quantum number?

(A) $\frac{7}{2}$

(B) 3

(C) $\frac{5}{2}$

(D) 2

(E) $\frac{3}{2}$

- Na: Fill up to 11 electrons:
  - 1s2 2s2 2p6 3s1
  - l = 0
  - S = ½
  - J = |l-s|

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(A) $^1S_0$ (B) $^2S_{\frac{1}{2}}$ (C) $^1P_0$

(D) $^2P_{\frac{1}{2}}$ (E) $^3P_{\frac{1}{2}}$

Selection Rules

- For a hydrogen-like atom to undergo a transition from a higher energy state to a lower energy state (thus emitting a photon), there are restrictions on the transitions that are allowed
- Specifically, the angular momentum quantum numbers must change:
  - $\Delta l = +1$ or -1
  - $\Delta m = +1, -1,$ or 0
- When working in spectroscopic notation:
  - $\Delta J = +1, -1,$ or 0
  - $\Delta s = 0$ (no restrictions due to spin, outside of Pauli)
- "Electric dipole transition"

Selection Rules - Examples

48. A transition in which one photon is radiated by the electron in a hydrogen atom when the electron's wave function changes from ψ_1 to ψ_2 is forbidden if ψ_1 and ψ_2

(A) have opposite parity
(B) are orthogonal to each other
(C) are zero at the center of the atomic nucleus
(D) are both spherically symmetrical
(E) are associated with different angular momenta

41. A $3p$ electron is found in the $^3P_{3/2}$ energy level of a hydrogen atom. Which of the following is true about the electron in this state?

(A) It is allowed to make an electric dipole transition to the $^2S_{1/2}$ level.
(B) It is allowed to make an electric dipole transition to the $^2P_{1/2}$ level.
(C) It has quantum numbers $\ell = 3$, $j = 3/2$, $s = 1/2$.
(D) It has quantum numbers $n = 3$, $j = \ell$, $s = 3/2$.
(E) It has exactly the same energy as it would in the $^3D_{3/2}$ level.

- Two examples:

Selection Rules - Examples

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(A) have opposite parity
(B) are orthogonal to each other
(C) are zero at the center of the atomic nucleus
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(E) are associated with different angular momenta

- Two examples:
- Spherically symmetric wave functions are both S-type orbitals
- There must be some change in angular momentum for radiation to occur

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(E) It has exactly the same energy as it would in the ${}^3D_{3/2}$ level.

- Need to use spectroscopic notation here as well!
  - S = 1/2, L = 1, J = L+S = 3/2
- (A) Seems possible
- (B) Angular momentum hasn't changed
- (C) Not true
- (D) An electron with spin 3/2?
- (E) Need an n=4 state to have a d-orbital

Atomic Physics Summary

- Know parts of the periodic table
- Understand and be able to recognize the spectrum and orbitals of hydrogen-like atoms
- Be able to calculate spectrum and ionization energies
- Know the order in which orbitals are filled
- Recognize spectroscopic notation
- Remember selection rules for dipole transitions
- Other topics
  - Basic chemistry
  - Types of chemical bonds
  - What causes spectra to change? (Pressure, Temperature, etc.)