CHEM 205 section 03

LECTURE #19 Thurs. March 13, 2008

LECTURE TOPICS:

TODAY'S CLASS: **finish Ch.7, start Ch.8**

NEXT CLASS: **finish Ch.8**

Describing atomic orbitals: quantum #s

DIFFERENT ORBITALS HAVE DIFFERENT PROPERTIES

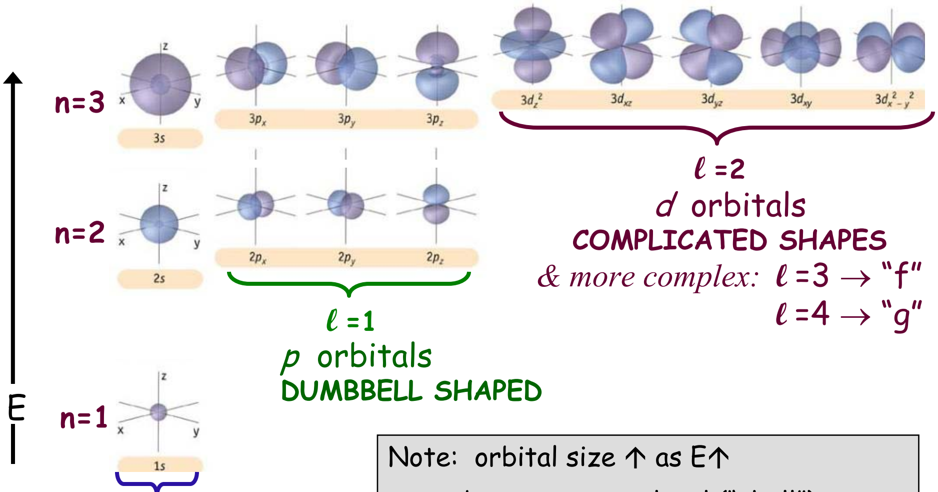
Each orbital is a solution to Schrödinger's eqn, describing the e^-'s energy

→ each orbital described by 3 "quantum numbers"

Quantum #	**Symbol**	**Describes…**	**Possible values**
Principal QN	n	**Energy level ("shell")** ***also n = # subshells/shell***	n = 1, 2, 3, … ∞
Angular Momentum QN	ℓ	**Orbital's shape**	ℓ = 0 to n-1
Magnetic QN	m_ℓ	**Orbital's orientation**	m_ℓ = $+\ell$ to $-\ell$

- In atoms with > 1 e^-, two or more e^-s can have same n value
  If so: in same "electron shell" & have similar (*OR* =) energy
- Electrons in a given shell: grouped into "subshells"
  based on shapes of their orbitals (defined by value of ℓ)
- Electrons in a given subshell: in same orbital (max. $2e^-$/orbital), *OR* in orbitals of different spatial orientation (defined by value of m_ℓ)

Thus: an e^- in an allowed E level of an H atom looks like 1 of…



ℓ =2
d orbitals
COMPLICATED SHAPES
& more complex: ℓ =3 → "f"
ℓ =4 → "g"

ℓ =1
p orbitals
DUMBBELL SHAPED

ℓ =0
s orbitals
SPHERICAL

Note: orbital size ↑ as E↑

- n: denotes energy level ("shell")
  PLUS: # subshells same as n value
- ℓ: denotes orbital shape
  PLUS: # nodal planes same as ℓ value

Zumdahl's Table 7.2

Quantum #s for H atom's 1st 4 electron shells

n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

Principal QN

Angular momentum QN

Subshell
orbitals of same type & energy = *degenerate*

Magnetic QNs:
One # for each suborbital in set
each has unique orientation, *i.e.,* direction it points

Degeneracy
= # orbitals with same energy (*i.e.,* # in subshell)

Similar:
K&T Table 7.1

GROUND STATE OF H ATOM = 1s orbital $n = 1, \ell = 0$

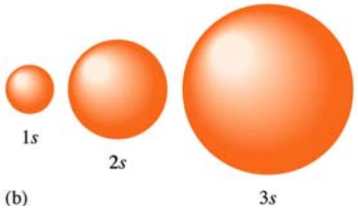
We'll now look at higher energy s-orbitals (other n values)...

...then look at other orbital types (other ℓ values)

Zumdahl's Figure 7.13: Hydrogen's 1*s*, 2*s* & 3*s* orbitals

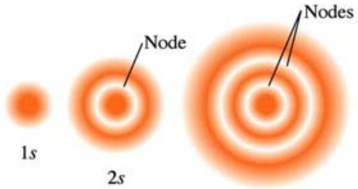
QUANTUM #s:	$n = 1, 2, 3\ldots$	ENERGY LEVEL or SHELL
	$\ell = 0$	SHAPE = SPHERICAL (s-orbitals)
	$m_\ell = 0$	ORIENTATION...no choice...spherical

Boundary Surface →
90% probability
of finding e^- inside
"size of the orbital"



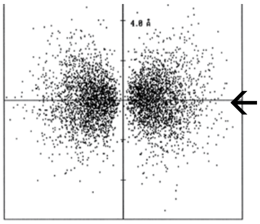
**Orbital size ↑
as energy ↑**

Cross-section →
electron probability
distribution "inside"
(hinted at in K&T Fig.7.15)



**# nodes ↑
as energy ↑**

Zumdahl's Figure 7.14:

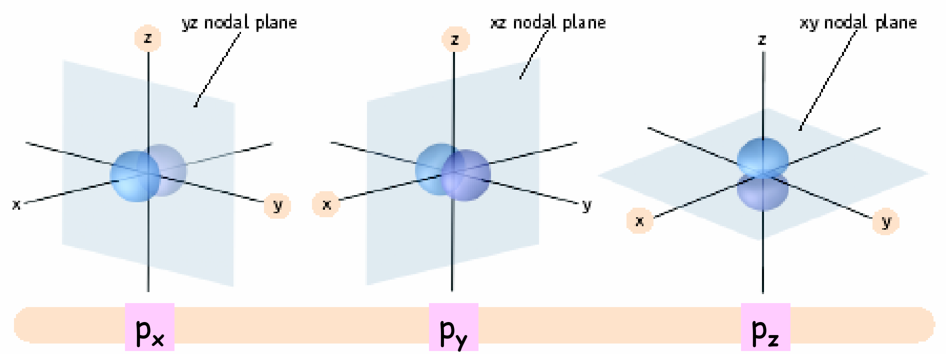


What are p orbitals like?

QN's: $n = 2$ & up, $\ell = 1$, $m_\ell = -1, 0, +1$

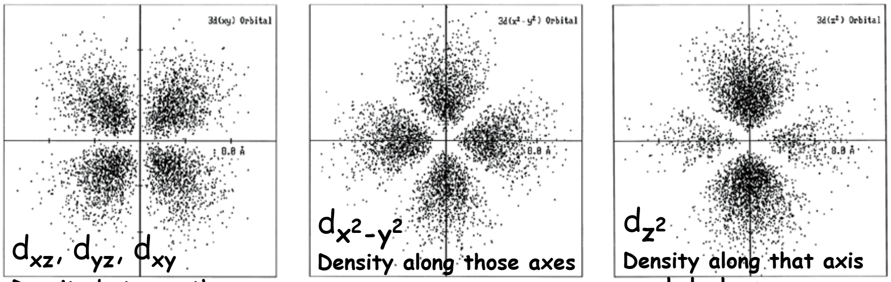
← **Cross-section** of $2p_x$ orbital
probability distribution
note: e^- density along x axis; node in yz plane
(recall we're talking about waves ⇨ have nodes!!)

Boundary surfaces: 90% probability e^- is in here... **K&T Figure 7.16**



d orbitals QN's: $n \geq 3$, $\ell = 2$, $m_\ell = -2, -1, 0, +1, +2$

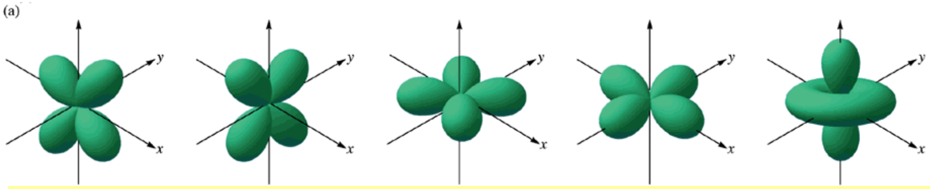
ℓ value ⇨ shape…&… ℓ = # nodal planes/surfaces



d_{xz}, d_{yz}, d_{xy}
Density between those axes

$d_{x^2-y^2}$
Density along those axes

d_{z^2}
Density along that axis
+ a hula-hoop



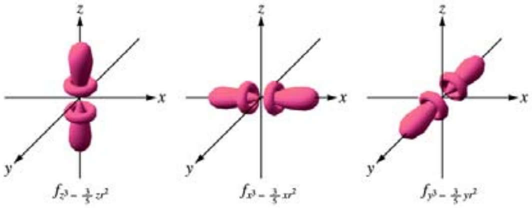
$3d_{xz}$ $3d_{yz}$ $3d_{xy}$ $3d_{x^2-y^2}$ $3d_{z^2}$

Zumdahl's Fig. 7.16 (see Kotz Fig. 7.15)

Zumdahl's Fig. 7.17: *f* orbitals …even more complex

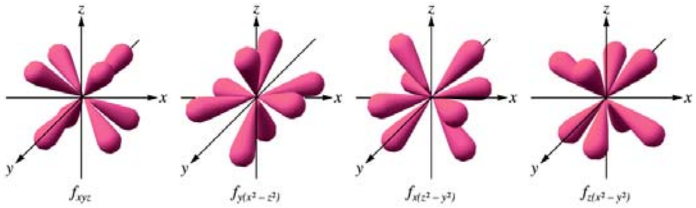
$n \geq 4$, $\ell = 3$, $m_\ell = -3, -2, -1, 0, +1, +2, +3$

3 nodal surfaces



All 7 f-orbitals represent e^-s at the same energy

= "degenerate" orbitals



You need to be able to draw the shapes of s, p & d orbitals… but don't worry about f orbitals.

THE STATE OF KNOWLEDGE ABOUT e^-s…

What IS known about ELECTRONS:

- Behave as standing waves (described by wavefunction, ψ)
- Exist near nucleus, in specific regions of space (defined by ψ^2)
- Can describe as being in specific "orbitals"
  but NOT Bohr's circular orbits (early idea was incorrect)…
- Energy of e^- determines which "orbital" it is in

What is NOT known:

- Exactly where an electron is at any moment
- HOW electrons move inside orbitals (…wave-particle duality?!?)

LUCKILY: knowing where it is **LIKELY** to find an e^- IS SUFFICIENT !

REMINDER: Why do we care where the electrons are?

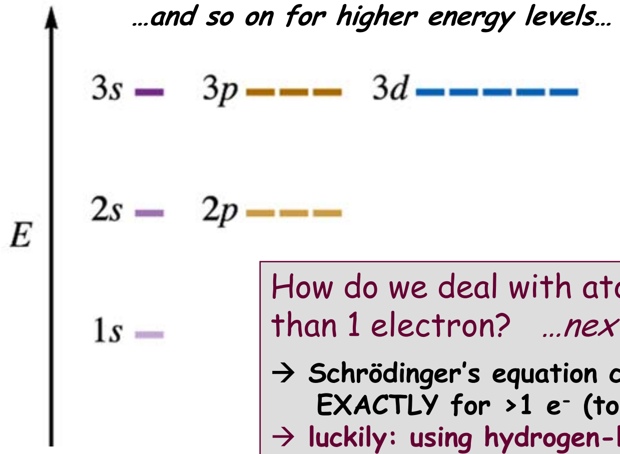
CHEMISTRY IS ALMOST ENTIRELY ABOUT ELECTRONS!

- **Reactions:** driven by attraction of e^-s to nuclei
- **Shapes of molecules:** determined by sharing of e^-s between nuclei
- **Interactions between molecules:** based on locations of electrons…

To understand physical & chemical behaviour of substances, we must "find" the electrons in the atoms.

Zumdahl's Figure 7.18: Relative energies of orbitals for the **hydrogen atom**

NOTE: H atom has 1 e^- …in ONE of these orbitals:



…and so on for higher energy levels…

How do we deal with atoms with more than 1 electron? *…next topic…*

→ **Schrödinger's equation cannot be solved EXACTLY for >1 e^- (too complicated!)**

→ **luckily: using hydrogen-like atomic orbitals works for other atoms…even in molecules…**

→ **difference: minor changes in energies**

Chapter 8: Atomic Electron Configurations & Chemical Periodicity

Treating atoms as +ve nuclei surrounded by e^-s in H-like orbitals…

…we can start EXPLAINING why things behave the way they do!

8.1 Electron spin
8.2 Pauli Exclusion Principle
8.3 Atomic Subshell Energies & Electron Assignments
8.4 Atomic Electron Configurations
8.5 Electron Configurations of Ions
8.6 Atomic Properties & Periodic Trends
8.7 Periodic Trends & Chemical Properties

CHAPTER GOALS:

- Understand the role magnetism plays in determining & revealing atomic structure
- Understand effective nuclear charge and its role in determining atomic properties
- Write the electron configurations for any element or monatomic ion
- Understand the fundamental physical properties of the elements & their periodic trends

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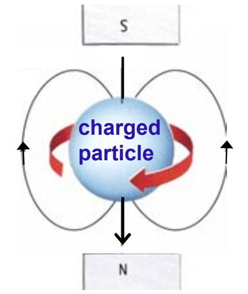
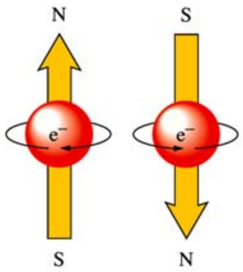
8.1 Electrons have a magnetic moment ⇨ must spin

PHYSICS: Spinning charges generate magnetic fields…



⇨ **Imagine e^-** (ignore its wave character…) **as a particle spinning like a top**



clockwise *vs.* counterclockwise
⇒ 2 "spin states"
⇒ $m_s = +\frac{1}{2}$ *or* $-\frac{1}{2}$
(4th quantum #)

Z's Fig. 7.19
K&T Fig. 8.1, 8.3

PHYSICAL SIGNIFICANCE OF THE 4th QUANTUM NUMBER:
Pauli exclusion principle: Any atomic orbital can "contain" 2 e^-, as long as the e^-s' spins are OPPOSITE

i.e.: **for any given E, math always yields 2 wavefunctions with same n, ℓ, m_ℓ** ⇨ same E, shape & orientation ⇨ same orbital! **but m_s value is different** ⇨ two unique electrons described considered as spinning opposite ways

Thus: with 4 QN's, can describe any electron in an atom
Q: Are the following sets of quantum #s reasonable?

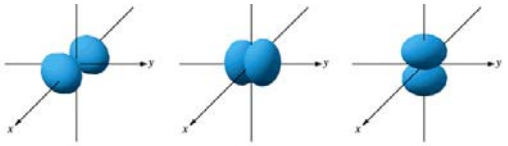
- IF $n = 2, \ell = 2, m_\ell = 1, m_s = +\frac{1}{2}$
- NOT POSSIBLE: ℓ can only have values from 0 up to (n-1)…
  …so… ℓ =2 is not possible for 2nd energy level (n=2)

  Significance? An e^- in the n=2 level cannot be in a *d* orbital…
  only allowed to be in *s* or *p* orbitals (ℓ =0 & 1)

- IF $n = 2, \ell = 1, m_\ell = 1, m_s = +\frac{1}{2}$ → this one IS possible:

energy level = 2
orbital type = *p*
orientation = p_y (? arbitrary choice – it's one of the 3…)
e^- spin = "up"

⇨ uniquely describes an e^- in one of the three 2*p* orbitals:



"$2p_x$" "$2p_y$" "$2p_z$"

8.2-8.4 Atomic Electron Configurations

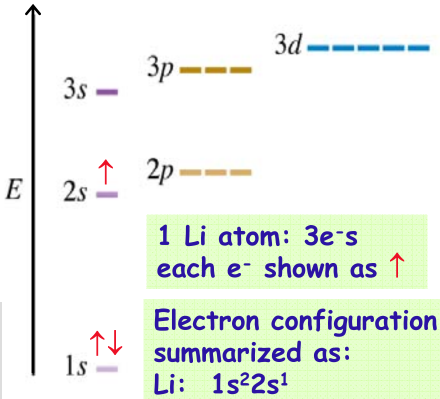
Determining where the e^-s are in a polyelectronic atom:

- Add them one-by-one into H-like orbitals (the aufbau principle…)
- Start with lowest E orbital
- maximum 2 e^- per orbital (Pauli exclusion principle…)
- then move to next, higher E orbital…

The aufbau principle
= the "building-up" principle

As p^+s are added 1-by-1 to the nucleus to build up the various elements, e^-s are similarly added to H-like orbitals.

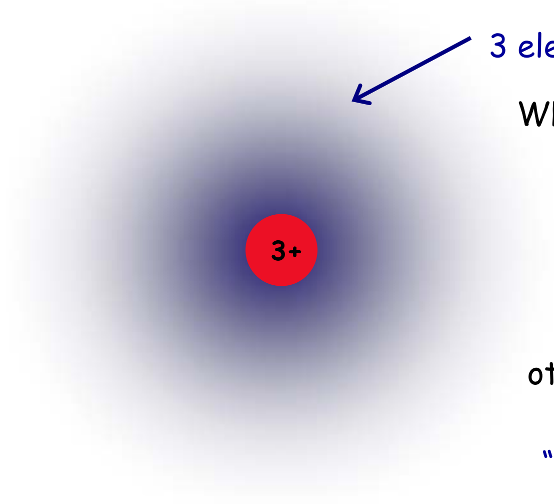
How do we understand the relative energies of the orbitals in a multi-electron atom?



1 Li atom: $3e^-$s each e^- shown as ↑

Electron configuration summarized as:
Li: $1s^2 2s^1$

A closer look: Imagine YOU are an electron in a Li atom…



3 electrons total

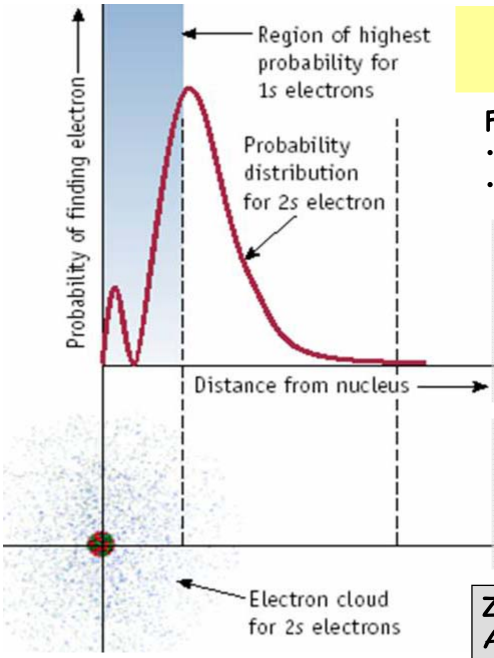
WHAT DOES OUTERMOST ELECTRON "SEE" ?

+ve charge of nucleus
(ATTRACTION)

…BUT…

other electrons in the way!
(REPULSION)

"screened" *or* "shielded"
by the other e^-s



Kotz Fig. 8.6

Z^* *or* Z_{eff}
Effective nuclear charge

For Lithium:

- 1 valence e^- in 2s orbital
- 2 core e^-s in 1s orbital

What does the valence e^- see?

- Most of the time: far away…

(+3 of nucleus)
− (2 screened by core e^-s)
+1 *since highly shielded*

- But when in innermost 2s region:

(+3 of nucleus)
− (0 screened by core e-s)
+3 *when not shielded*

Z^* = between +1 → +3
Average = 1.28 for Li's 2s e^-
Closer to *highly-shielded extreme…*

EFFECTIVE NUCLEAR CHARGE: Z_{eff} *or* Z^*

Table 8.2

Atom	$Z^*(2s)$	$Z^*(2p)$
Li	1.28	
B	2.58	2.42
C	3.22	3.14
N	3.85	3.83
O	4.49	4.45
F	5.13	5.10

Notice:
e^-s in *s*-orbitals always feel higher Z* than e^-s in *p*-orbitals
⇨ because *s*-orbitals penetrate closer to the nucleus than *p*s!
⇨ **explains why *s* orbitals are lower E than *p*s in same E level**

Calculating REAL average values of Z* is difficult, but possible.
Simple to estimate instead by considering "highly shielded extreme":

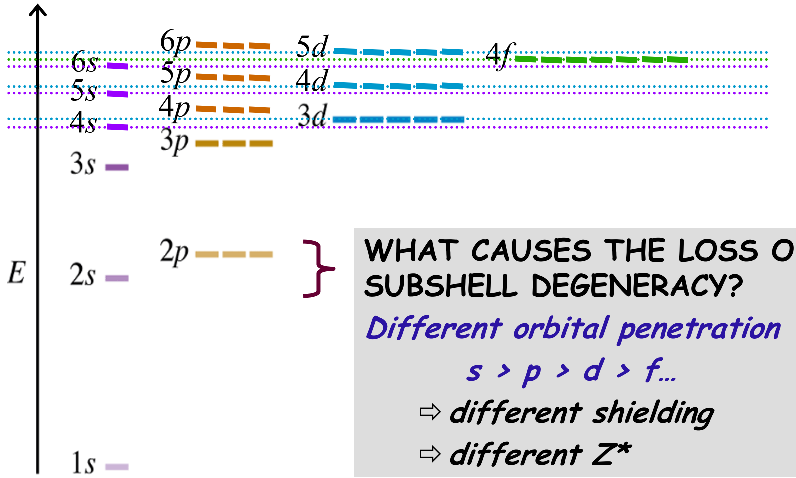
- **EFFECTIVE NUCLEAR CHARGE (Z_{eff} or Z*)**
  = average nuclear charge felt by a particular e^- (*e.g.*, each valence e^-)
  because of shielding by other electrons

Highly shielded extreme:
(not an official term)

Z_{eff}^{min} = (nuclear charge) – (# core e^-s)

Relative Es of atomic orbitals for multi-e^- atoms

- ordering shown here: based on experimental data
- as ↑ in energy, levels get closer & closer together
  ⇨ not all "n=4" orbitals higher in E than "n=3" orbitals…*etc.*

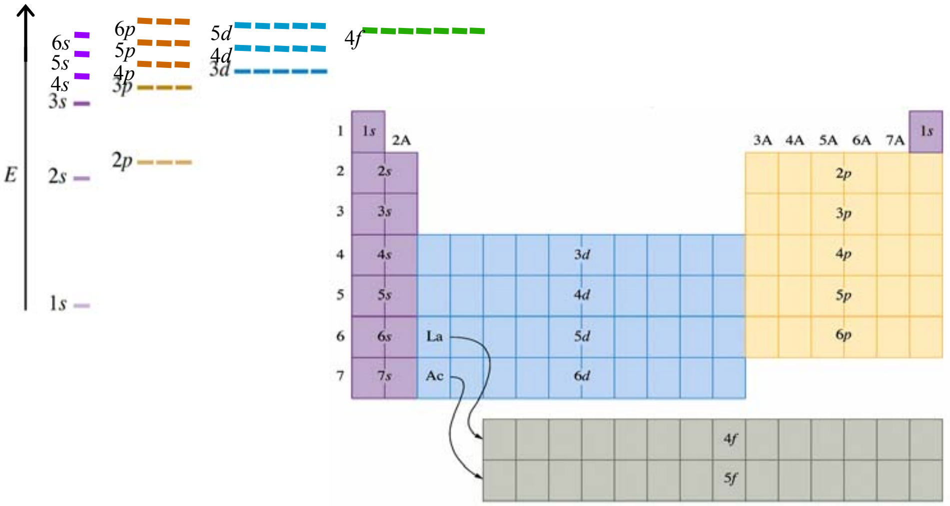


WHAT CAUSES THE LOSS OF SUBSHELL DEGENERACY?
Different orbital penetration
s > p > d > f…
⇨ *different shielding*
⇨ *different Z**

HOW TO REMEMBER ORDER OF ORBITAL ENERGIES?

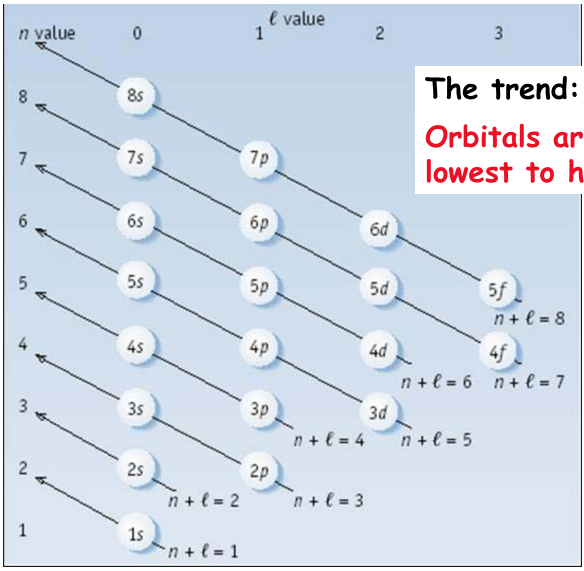
1.) use " n + ℓ " zig-zag diagram (Kotz Fig. 8.5 – next slide)

2.) learn to read the periodic table (recommended…)



- # elements/block indicates orbital type: 2 ⇨ s, 6 ⇨ p, 10 ⇨ d, 14 ⇨ f
- orbitals "seen" on P.T. from lower→higher E: 1st d is 3d, 1st f is 4f…

Fig.8.5: Zig-zag memory aid for relative orbital energies



The trend:

Orbitals are filled in order from lowest to highest " n + ℓ " value

Many people find this diagram useful…

But:
less to memorize if simply use the periodic table…

"ELECTRON CONFIGURATION"
(which orbitals occupied…)

"ORBITAL BOX DIAGRAM"
(boxes with e^-s & spin)

H: $1s^1$

orbital name

occupancy (# e^- in it!)

1s	2s	2p		
↑				

Degenerate set of orbitals (same subshell)

		1s	2s	2p		
He:	$1s^2$	↑↓				
Li:	$1s^22s^1$	↑↓	↑			
Be:	$1s^22s^2$	↑↓	↑↓			
B:	$1s^22s^22p^1$	↑↓	↑↓	↑		
C:	$1s^22s^22p^2$	↑↓	↑↓	↑	↑	

Degenerate set?
- must fill each orbital ½-full before adding 2nd e^- to any…
= HUND's rule

Hund's rule: the lowest energy electron configuration for an atom has the maximum number of unpaired e^-s allowed by the Pauli principle in a particular set of degenerate orbitals.

(21)

		1s	2s	2p		
He:	$1s^2$	↑↓				
Li:	$1s^22s^1$	↑↓	↑			
Be:	$1s^22s^2$	↑↓	↑↓			
B:	$1s^22s^22p^1$	↑↓	↑↓	↑		
C:	$1s^22s^22p^2$	↑↓	↑↓	↑	↑	
N:	$1s^22s^22p^3$	↑↓	↑↓	↑	↑	↑
O:	$1s^22s^22p^4$	↑↓	↑↓	↑↓	↑	↑
F:	$1s^22s^22p^5$	↑↓	↑↓	↑↓	↑↓	↑
Ne:	$1s^22s^22p^6$	↑↓	↑↓	↑↓	↑↓	↑↓

FULL: n=1

Noble gases: FULL VALENCE SHELLS

FULL: n=2

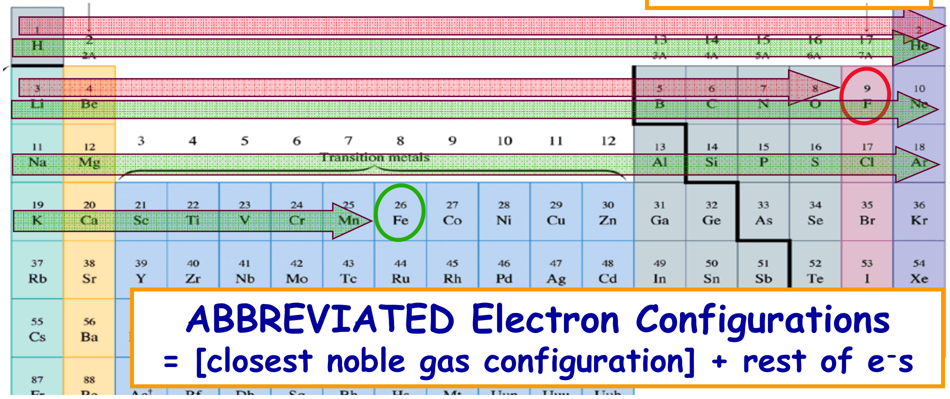
(22)

Using the periodic table to predict e^- configurations

- **Add e^-s to your configuration 1 at a time, by counting across as Z ↑**
  - because when Z goes up by 1, the number of electrons goes up by 1…
- **To remember the orbital filling order (relative energies):**
  - # elements/block indicates orbital type: 2 ⇨ s, 6 ⇨ p, 10 ⇨ d, 14 ⇨ f
  - "orbitals seen" on P.T. from lower→higher E: 1st d is 3d, 1st f is 4f…

Fluorine F: $1s^2 2s^2 2p^5$ ⇨ F: $[He]2s^2 2p^5$

Iron Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \underline{3}d^6$ ⇨ Fe: $[Ar]4s^2 3d^6$



ABBREVIATED Electron Configurations

= [closest noble gas configuration] + rest of e^-s

Valence Electrons

Lower E electrons are called <u>core electrons</u>.

- highest energy, outermost electrons in <u>unfilled</u> shells
- usually e^-s with highest principle Q.N.

…but not always (relative orbital Es…)

Element	Configuration	Valence
Cl	$1s^2 2s^2 2p^6$ $3s^2 3p^5$	7 (in n=3)
	core **valence**	
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6$ $4s^2 3d^6$	8 (in n=3&4)

Note: our Hund's rule predictions of e^- configurations do not match some exp'tal conclusions for some transition metals (*e.g.*, Cr, Cu, Pt…)

↳ *based on colours absorbed/emitted, degree of interaction with magnets…*

You do <u>**not**</u> need to memorize these exceptions (seen in text) for Chem 205.

Predicted for Cu:	$[Ar]$ $4s^2 3d^9$	11 (in n=3&4)
Observed for Cu:	$[Ar]$ $4s^1 3d^{10}$	11 (in n=3&4)

ASSIGNED READINGS

- **BEFORE NEXT CLASS:**

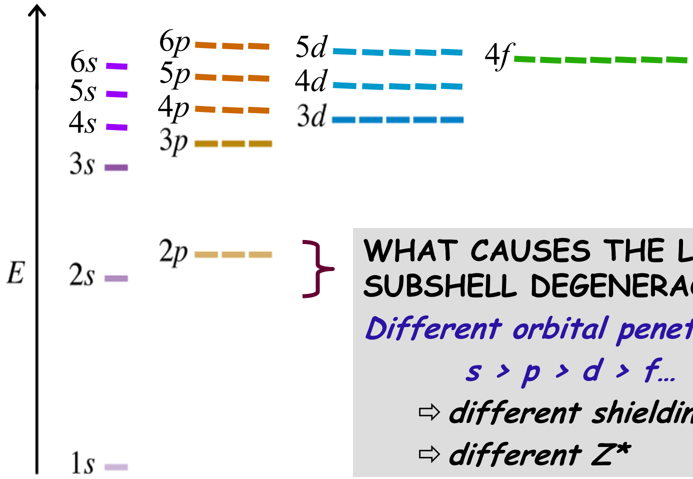
read up to & including Ch.8.4

master: orbital names, shapes & energies,
assigning/using quantum numbers

practice: electron configurations of atoms/ions
identifying valence *vs.* core electrons
using orbital-box diagrams

Extra slides: More detail

…to help understand relative energies of orbitals



WHAT CAUSES THE LOSS OF SUBSHELL DEGENERACY?

Different orbital penetration

s > p > d > f…

⇨ *different shielding*

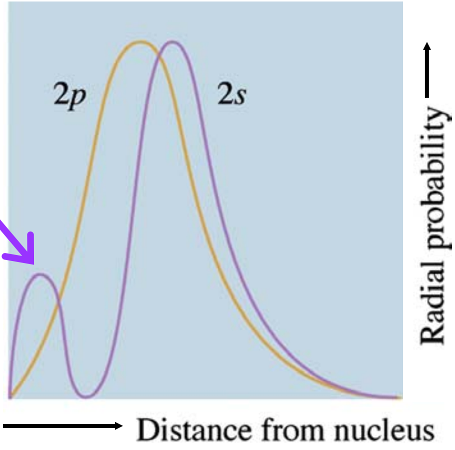
⇨ *different Z^**

Relative energies <u>in same level</u>: s < p < d < f…

Based on effective nuclear charge felt by e^-s there…

Zumdahl's Figure 7.20:

2s e^- wave exists partly in region occupied by 1s e^-s… more so than 2p orbital does → higher "penetration"



PHYSICAL MEANING:

2s orbital is a bit <u>closer</u> to nucleus than 2p orbital…

…sometimes in same space as the 1s e^-s (the "core" e^-s)

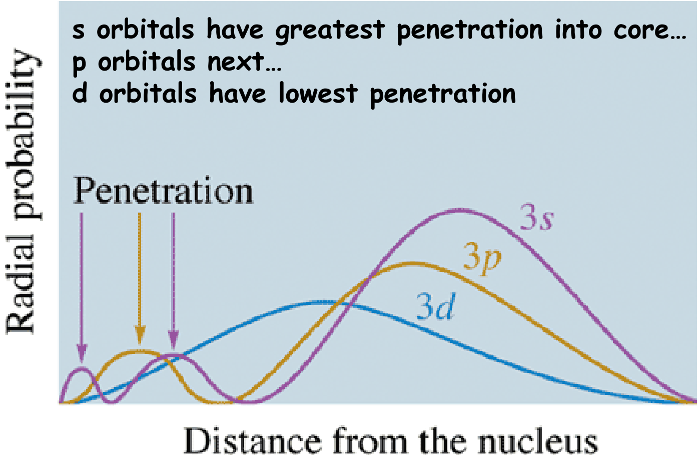
⇨ thus: 2s a bit <u>less shielded by core e^-s</u> than 2p

Implies: 2s e^- feels stronger electrostatic attraction to nucleus…

(2s sees higher EFFECTIVE NUCLEAR CHARGE than 2p)

THUS: 2s orbital lower in E than 2p

PENETRATION explains relative orbital energies: s < p < d …



s orbitals have greatest penetration into core…
p orbitals next…
d orbitals have lowest penetration

Zumdahl's Figure 7.21b

→ see Kotz p.342 for similar explanations