ELECTRONS IN CONFIGURATIONS

Learning objectives

- o Explain the difference between a continuous spectrum and a line spectrum.
- o Explain the difference between an emission and an absorption spectrum.
- o Use the concept of quantized energy states to explain atomic line spectra.
- o Given an energy level diagram, predict wavelengths in the line spectrum, and vice versa.
- o Define and distinguish between shells, subshells, and orbitals.
- o Explain the relationships between the quantum numbers.
- o Use quantum numbers to label electrons in atoms.
- o Describe and compare atomic orbitals given the n and ℓ quantum numbers.
- o List a set of subshells in order of increasing energy.
- o Write electron configurations for atoms in either the subshell or orbital box notations.
- o Write electron configurations of ions.
- o Use electron configurations to predict the magnetic properties of atoms.

Lecture outline

The quantum theory was used to show how the wavelike behavior of electrons leads to quantized energy states when the electrons are bound or trapped. In this section, we'll use the quantum theory to explain the origin of spectral lines and to describe the electronic structure of atoms.
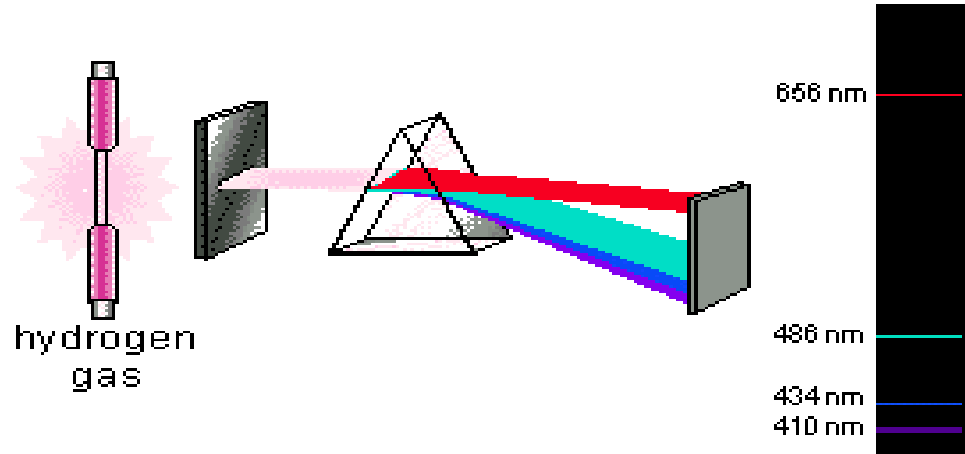
Emission Spectra

- o experimental key to atomic structure: analyze light emitted by high temperature gaseous elements
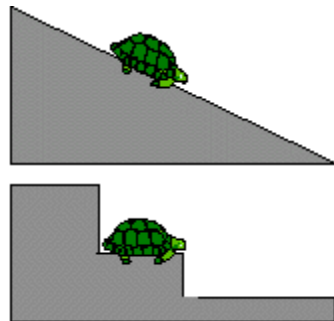 - ▪ experimental setup: spectroscopy
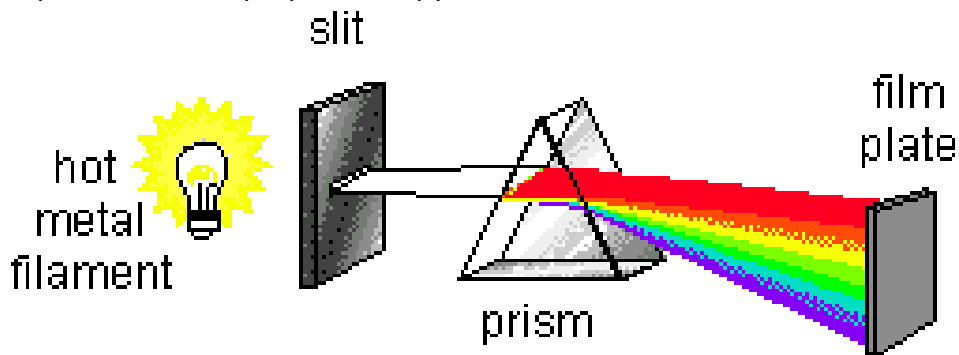
  - ▪ atoms emit a characteristic set of discrete wavelengths – not a continuous spectrum!
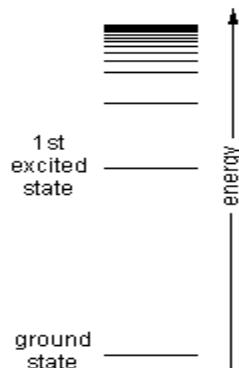
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- atomic spectrum can be used as a "fingerprint" for an element
  - o hypothesis: if atoms emit only discrete wavelengths, maybe atoms can have only discrete energies
  - o an analogy

A turtle sitting on a ramp can have any height above the ground- and so, any potential energy

A turtle sitting on a staircase can take on only certain discrete energies

- energy is required to move the turtle up the steps (absorption)
- energy is released when the turtle moves down the steps (emission)
- only discrete amounts of energy are absorbed or released (energy is said to be **quantized**)
  - o energy staircase diagram for atomic hydrogen

- bottom step is called the **ground state**
- higher steps are called **excited states**

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- o computing line wavelengths using the energy staircase diagram
- o computing energy steps from wavelengths in the line spectrum
- o summary: line spectra arise from transitions between discrete (**quantized**) energy states

The quantum mechanical atom

- o Electrons in atoms have quantized energies
  - ▪ Electrons in atoms are bound to the nucleus by electrostatic attraction
  - ▪ Electron waves are standing matter waves
  - ▪ standing matter waves have quantized energies, as with the "electron on a wire" model
- o Electron standing matter waves are 3 dimensional
  - ▪ The electron on a wire model was one dimensional; one quantum number was required to describe the state of the electron
  - ▪ A 3D model requires three quantum numbers
  - ▪ A three-dimensional standing matter wave that describes the state of an electron in an atom is called an **atomic orbital**
- o The energies and mathematical forms of the orbitals can be computed using the **Schrödinger equation**
  - ▪ quantization isn't assumed; it arises naturally in solution of the equation
  - ▪ every electron adds 3 variables (x, y, z) to the equation; it's very hard to solve equations with lots of variables.
  - ▪ energy-level separations computed with the Schrödinger equation agree very closely with those computed from atomic spectral lines

Quantum numbers

- o Think of the quantum numbers as addresses for electrons
- o the principal quantum number, n
  - ▪ determines the size of an orbital (bigger n = bigger orbitals)
  - ▪ largely determines the energy of the orbital (bigger n = higher energy)
  - ▪ can take on integer values n = 1, 2, 3, ..., ∞
  - ▪ all electrons in an atom with the same value of n are said to belong to the same **shell**
  - ▪ Spectroscopists use the following names for shells

n	shell name	n	shell name
1	K	5	O
2	L	6	P
3	M	7	Q
4	N		

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o the azimuthal quantum number, ℓ
- designates the overall shape of the orbital within a shell
- affects orbital energies (bigger ℓ = higher energy)
- all electrons in an atom with the same value of ℓ are said to belong to the same **subshell**
- only integer values between 0 and n-1 are allowed
- sometimes called the orbital angular momentum quantum number
- Spectroscopists use the following notation for subshells

ℓ	subshell name
0	s
1	p
2	d
3	f

o the magnetic quantum number, m_ℓ
- determines the orientation of orbitals within a subshell
- does not affect orbital energy (except in magnetic fields!)
- only integer values between $-\ell$ and $+\ell$ are allowed
- the number of m_ℓ values within a subshell is the number of orbitals within a subshell

ℓ	possible values of m_ℓ	number of orbitals in this subshell
0	0	1
1	-1, 0, +1	3
2	-2, -1, 0, +1, +2	5
3	-3, -2, -1, 0, +1, +2, +3	7

o the spin quantum number, m_s
- several experimental observations can be explained by treating the electron as though it were spinning
- spin makes the electron behave like a tiny magnet
- spin can be clockwise or counterclockwise
- spin quantum number can have values of +1/2 or -1/2

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Electron configurations of atoms

- o a list showing how many electrons are in each orbital or subshell in an atom or ion
- o subshell notation: list subshells of increasing energy, with number of electrons in each subshell as a superscript
  - ▪ examples:
    - □ $1s^2\,2s^2\,2p^5$ means "2 electrons in the 1s subshell, 2 electrons in the 2s subshell, and 5 electrons in the 2p subshell"
    - □ $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$ is an electron configuration with 15 electrons total; 2 electrons have n=1 (in the 1s subshell); 8 electrons have n=2 (2 in the 2s subshell, and 6 in the 2p subshell); and 5 electrons have n=3 (2 in the 3s subshell, and 3 in the 3p subshell).
- o ground state configurations fill the lowest energy orbitals first
- o electron configurations of the first 11 elements, in subshell notation. Notice how configurations can be built by adding one electron at a time.

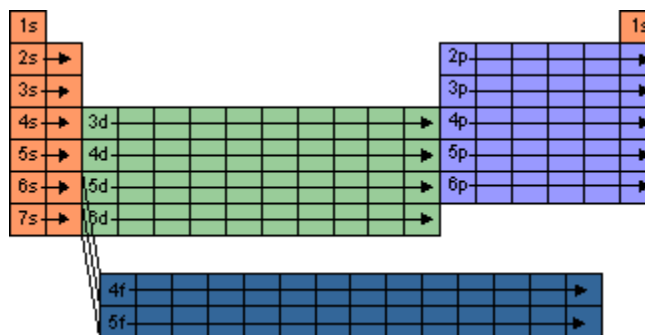| atom	Z	ground state electronic configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2\,2s^1$
Be	4	$1s^2\,2s^2$
B	5	$1s^2\,2s^2\,2p^1$
C	6	$1s^2\,2s^2\,2p^2$
N	7	$1s^2\,2s^2\,2p^3$
O	8	$1s^2\,2s^2\,2p^4$
F	9	$1s^2\,2s^2\,2p^5$
Ne	10	$1s^2\,2s^2\,2p^6$
Na	11	$1s^2\,2s^2\,2p^6\,3s^1$

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Writing electron configurations

- o strategy: start with hydrogen, and build the configuration one electron at a time (the Aufbau principle)
    1. fill subshells in order by counting across periods, from hydrogen up to the element of interest:

    2. rearrange subshells (if necessary) in order of increasing n & l

- o examples: Give the ground state electronic configurations for:
    - Al
    - Fe
    - Ba
    - Hg
- o watch out for d & f block elements; orbital interactions cause exceptions to the Aufbau principle
    - half-filled and completely filled d and f subshells have extra stability
- o Know these exceptions to the Aufbau principle in the 4th period. (There are many others at the bottom of the table, but don't worry about them now.)

exception	configuration predicted by the Aufbau principle	true ground state configuration
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Electron configurations including spin

- o unpaired electrons give atoms (and molecules) special magnetic and chemical properties
- o when spin is of interest, count unpaired electrons using orbital box diagrams

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- examples of ground state electron configurations in the orbital box notation that shows electron spins.

atom	orbital box diagram

B — 1s [↓↑] 2s [↓↑] 2p [↑][ ][ ]

C — 1s [↓↑] 2s [↓↑] 2p [↑][↑][ ]

N — 1s [↓↑] 2s [↓↑] 2p [↑][↑][↑]

O — 1s [↓↑] 2s [↓↑] 2p [↓↑][↑][↑]

F — 1s [↓↑] 2s [↓↑] 2p [↓↑][↓↑][↑]

Cl — 1s [↓↑] 2s [↓↑] 2p [↓↑][↓↑][↓↑] 3s [↓↑] 3p [↓↑][↓↑][↑]

Mn — 1s [↓↑] 2s [↓↑] 2p [↓↑][↓↑][↓↑] 3s [↓↑] 3p [↓↑][↓↑][↓↑]

... 3d [↑][↑][↑][↑][↑] 4s [↓↑]

- **drawing orbital box diagrams –**
- write the electron configuration in subshell notation
- draw a box for each orbital.
    - Remember that s, p, d, and f subshells contain 1, 3, 5, and 7 degenerate orbitals, respectively.
    - Remember that an orbital can hold 0, 1, or 2 electrons only, and if there are two electrons in the orbital, they must have opposite (paired) spins (Pauli principle)
- within a subshell (depicted as a group of boxes), spread the electrons out and line up their spins as much as possible (Hund's rule)
- the number of unpaired electrons can be counted experimentally
    - configurations with unpaired electrons are attracted to magnetic fields (paramagnetism)
    - configurations with only paired electrons are weakly repelled by magnetic fields (diamagnetism)

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Core and valence electrons

o chemistry involves mostly the shell with the highest value of principal quantum number, n, called the valence shell

o the noble gas core under the valence shell is chemically inert

o simplify the notation for electron configurations by replacing the core with a noble gas symbol in square brackets:

		Examples of electron configurations written with the core/valence notation		
atom	full configuration	core	valence configuration	full configuration using core/valence notation
O	$1s^2\ 2s^2\ 2p^4$	He	$2s^2\ 2p^4$	$[He]\ 2s^2\ 2p^4$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	Ne	$3s^2\ 3p^5$	$[Ne]\ 3s^2\ 3p^5$
Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	Ne	$3s^2\ 3p^1$	$[Ne]\ 3s^2\ 3p^1$

o electrons in d and f subshells outside the noble gas core are called **pseudocore electrons**

		Examples of electron configurations containing pseudocore electrons		
atom	core	pseudocore	valence	full configuration
Fe	Ar	$3d^6$	$4s^2$	$[Ar]\ 3d^6\ 4s^2$
Sn	Kr	$4d^{10}$	$5s^2\ 5p^2$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^2$
Hg	Xe	$4f^{14}\ 5d^{10}$	$6s^2$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2$
Pu	Rn	$5f^6$	$7s^2$	$[Rn]\ 5f^6\ 7s^2$