UNIT 2 – STRUCTURE & PROPERTIES

The Quantum Mechanical Model of the Atom

QUANTUM NUMBERS

During and subsequent to Bohr's work, others continued to probe the behaviour of light emitted or absorbed by the atom. As a result, additional components were added to Bohr's model to improve its ability to explain the behaviours observed. This led to the introduction of quantum numbers, in addition to Bohr's Principle Quantum Number.

Principal Quantum Number, n

- Goes back to Bohr model which labeled the shells
- Today called Principal Quantum Number, i.e. n=1,2,3......etc.
- n=1 is closest to the nucleus with the lowest energy
- Relates primarily to the main energy of an electron
  e.g. Fig. 1 "energy staircase" where energy levels are like unequal steps

Secondary Quantum Number, l

- Michelson found that the spectrum of H was composed of more than one line (experimental observation using spectrometry indicated that main lines of hydrogen spectra composed of more than one line – line splitting (Michelson, 1891)
- Sommerfeld (1915) used elliptical orbits to extend the knowledge of the time by explaining Michelson's work
- He introduced the concept of there being additional electron subshells (or sublevels) that formed part of the energy levels and used the concept of the secondary quantum number to describe this concept
- I.e. each energy "step" was a group of several little steps

- "l" relates to the shape of the electron orbit and the number of values for l equals the volume of n
- i.e. if n=3, then l=0,1,2
  as letters: l = s, p, d, f, g

Magnetic Quantum Number, m_l

- it was observed that if a gas discharge tube was placed near a strong magnet, some single lines split into new lines
- called normal Zeeman effect after Zeeman who 1st observed this (1897)
- this was explained by Sommerfeld & Debye (1916) who thought that orbits may exist at varying angles and that the energies may be different when near strong magnets
- for each value of l, m_l can vary from $-l$ to $+l$ (each value represents a different orientation)
- i.e. if l=1 then m_l can be $-1,0$ or $+1$
  if l=2 then m_l can be $-2,-1,0,+1$, or $+2$

Summary: The magnetic quantum number m_l , relates to the direction of the orbit of the electrons. The number of values of m_l represents the number of orientations of the orbits that we can have.

Spin Quantum Number, m_s

- needed to explain additional spectral line-splitting & different kinds of magnetism
- ferromagnetism-associated with substances containing Fe, Co & Ni
- paramagnetism-weak attraction to strong magnets (individual atoms vs. collection of atoms)
- paramagnetism couldn't be explained until Wolfgang Pauli suggested that electrons spin on their axis (1925)
- could spin only 2 ways (clockwise vs. counterclockwise) and he used only 2 numbers to describe this:
  $m_s = +1/2$ (clockwise) or $-1/2$ (counterclockwise)
- opposite pairs of electron spins represent a stable arrangement

- when electrons are paired – spin in opposite directions – the magnetic field is neutralized, while an individual electron spin can be affected by a magnet

Shape of Orbitals

- using the quantum numbers gives an ordered description of the electrons in a particular atom
- the secondary quantum number, l, is presented as s, p, d, and f to represent the shape of the orbitals

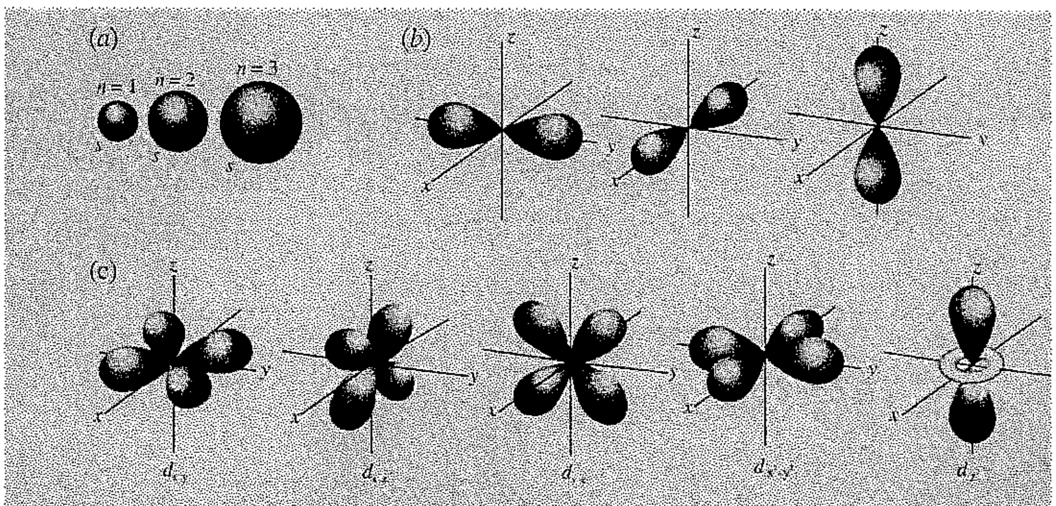


Figure 3.1 Geometry of orbitals in the *s*, *p*, and *d* subshells. Orbitals represent the volume of space around a nucleus in which is most probably located. (*a*) Orbitals in the *s* subshells are spherical in all shells. (*b*) The *p* subshell contains three different bilob oriented along orthogonal *x*, *y*, and *z* axes. (*c*) The *d* subshell contains five orbitals. The d_{xy}, d_{xz}, and d_{yz} orbitals are quadralob in the *xy*, *xz*, and *yz* planes, respectively, so as to bisect the angles between the orthogonal axes. The $d_{x^2-y^2}$ orbital forms a qu shape with lobes aligned along the *x* and *y* axes. The d_{z^2} orbital forms a torus with a bilobate shape aligned along the *z* axis.

Summary

Qunatum Number	Symbol	Possible Values	Property
	n		
	l		
	m_l		
	m_s		

Write the set of quantum numbers for each electron in Hydrogen, Helium and Lithium.

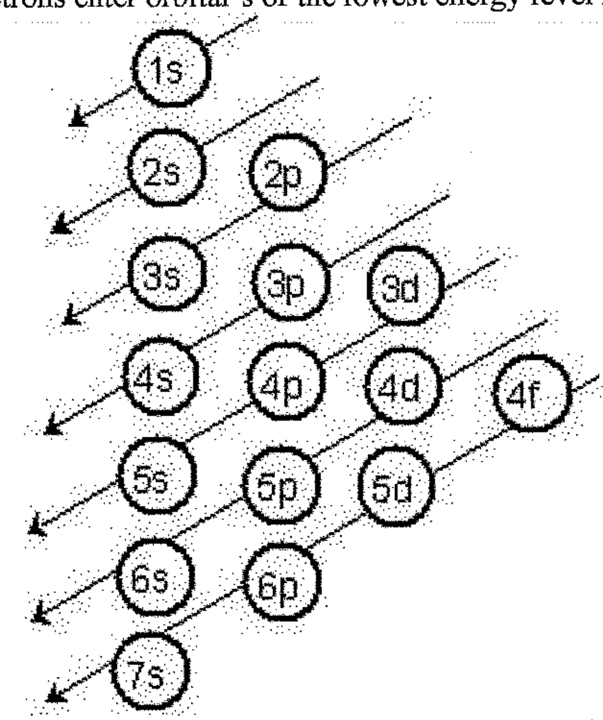
Hydrogen:

Helium:

Lithium:

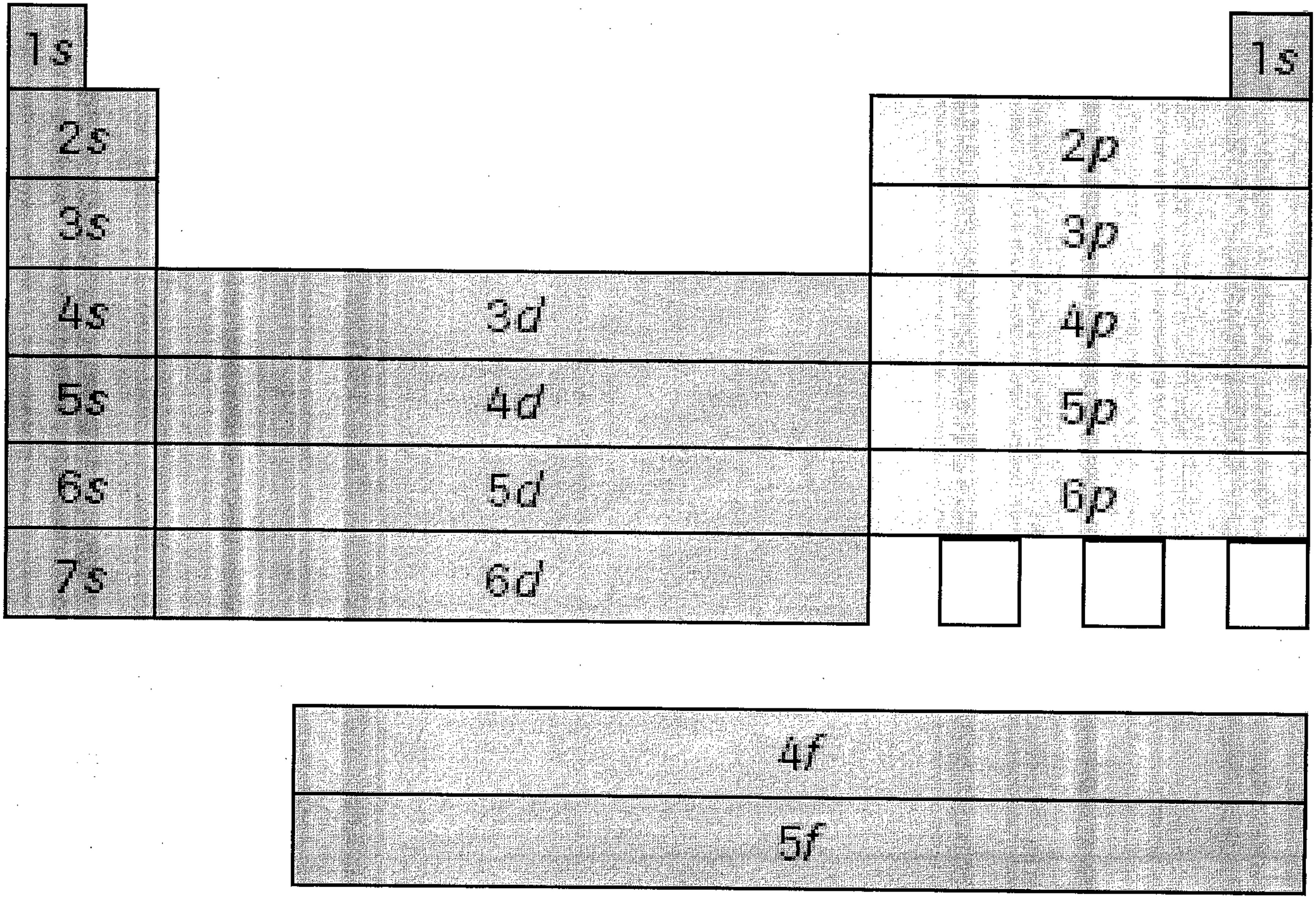
There are three rules that apply to creating an energy-level diagram:

1) Pauli Exclusion Principle: an orbital may only have 2 electron at the most
2) Aufbau Principle: electrons enter orbital's of the lowest energy level first



3) Hund's Rule: when electron occupy orbital's of equal energy, one electron enters each orbital until all orbital contain one electron (with parallel spins)

Classification of Elements by Sublevels Being Filled



Configurations , Quantum Numbers, and Energy Levels

1. Identify the electron configuration for the neutral atom whose valence electron has the following quantum numbers. An electron with a spin of +½ indicates the first electron in an atomic orbital. Use the periodic table at the back of your text for assistance.

Element	n	l	m_l	m_s	Element	n	l	m_l	m_s
(a)	2	0	0	-½	(b)	4	2	+2	+½
(c)	3	2	+2	+½	(d)	3	1	+1	-½
(e)	5	1	0	+½	(f)	2	1	0	+½
(g)	4	2	-1	-½	(h)	6	1	0	-½
(i)	3	2	0	-½	(j)	6	0	0	-½
(k)	2	1	-1	-½	(l)	2	1	0	-½
(m)	4	0	0	+½	(n)	5	0	0	+½
(o)	4	1	+1	+½	(p)	2	1	-1	+½

2. Draw an energy level diagram for a neutral bromine atom.

3. Assign quantum numbers for each electron in the 4s, 3d, and 4p orbitals of the bromine atom.

4. Draw energy level diagrams and electron configurations for the following neutral atoms. Remember to consider the "anomalous" electron configurations for copper and chromium. Explain why copper and chromium have the configurations that they do?
   - (a) phosphorus
   - (b) calcium
   - (c) vanadium
   - (d) scandium
   - (e) titanium
   - (f) chromium
   - (g) iron
   - (h) cobalt
   - (i) nickel
   - (j) copper
   - (k) zinc

Addresses/ Electron Configuration

- the location of each electron can be described in a number of ways, like an address …

Full Electron Configuration Notation

Indicate same number of e- as atomic number

e.g. $_{12}Mg$ $1s^2, 2s^2, 2p^6, 3s^2$

Condensed Electron Configuration Notation

Place previous noble gas in square brackets and then continue with number of e-

e.g. $_{12}Mg$ [Ne] $3s^2$

Orbital Representation

Use arrows as e- and boxes to represent orbitals

e.g. $_{12}Mg$ 1s $\boxed{\uparrow\downarrow}$ 2s $\boxed{\uparrow\downarrow}$ 2p $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ 3s $\boxed{\uparrow\downarrow}$

Ions – the electron configuration matches the number of e- in neutral and charged atoms
e.g. $_{12}Mg^{2+}$ $1s^2, 2s^2, 2p^6$ (remember - two e- are given up by Mg^{2+} ion)

Isoelectronic Elements

Main group elements form ions with noble gas configurations. Three elements preceding and three elements following a noble gas can be isoelectronic (have the same e- configuration) to each other if they gain or lose enough e- e.g. N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, Al^{3+} all have the same e- configuration $1s^2, 2s^2, 2p^6$

Exceptions to E- Configuration Patterns

The e- configurations of several elements differ slightly from the predicted pattern

e.g. $_{24}Cr$ predicted [Ar] $4s^2\ 3d^4$ observed [Ar] $4s^1\ 3d^5$

e.g. $_{29}Cu$ predicted [Ar] $4s^2\ 3d^9$ observed [Ar] $4s^1\ 3d^{10}$

one or two e- shift from one sublevel to another of similar energy to create a stable configuration

*** orbitals are most stable when full or half full**

Transitional Metal Cations

– do not form ions with noble gas configurations as they would have to lose too many e-

- e- are removed from the sublevels with the highest "n" value, thus outer "s" e- move 1st

e.g. $_{25}Mn$ [Ar] $4s^2\ 3d^5$ becomes $_{25}Mn$ [Ar] $4s^0\ 3d^5$

- only after the outer "s" e- are removed than the e- are taken from "d"

e.g. $_{26}Fe$ [Ar] $4s^2\ 3d^6$ becomes $_{26}Fe^{2+}$ [Ar] $4s^0\ 3d^6$ or $_{26}Fe^{3+}$ [Ar] $4s^0\ 3d^5$

The Valence Shell

For main group elements (s and p block elements):

a) only the v.e- can take part in chemical reactions

b) the number of e- is equal to the last number of the group number except He (in Group 18 because it has a full shell)

The valence shell is the group of e- in the atom with the highest value of "n"

e.g. Group 1 valence shell configuration ns^1 (H, Li, Na, K, Rb, Cs, Fr)

In the transition elements the ns e- and the (n-1)d e- both take part in reactions.

The Excited State

If energy is put into an atom, an e- can be transferred to a higher energy orbital, producing an excited state, as the e- falls back down to its usual energy orbital or ground state, it releases the excess energy in the form of light

Quantum Numbers

1. Principle Quantum Number "n" (n=1,2,3,4) the energy level
2. Orbital Quantum Number "l" (0-(n-1)) – the sublevels are shapes 0=s, 1=p, 2=d, 3=f
3. Magnetic Quantum Number "m_l" – determines the direction of the orbital in space
4. Spin Quantum Number "m_s" (+/- ½) - the spin of the e-

PRACTICE

1. Write the electron configurations for the 1st 20 elements, plus Fe, Co, Br, Sn & Br.

2. What do you notice about elements that are in the same family (column)?

3. How many unpaired electrons are there in boron? In fluorine? In neon?

4. How many electrons are in the highest occupied energy level of these atoms:
   a) barium b) sodium c) aluminum d) oxygen

5. Arrange the following sublevels in order of decreasing energy:
   2p, 4s, 3s, 3d and 3p

6. Draw energy level diagrams for: a) V b) Cs^+ c) P^{3-}

7. Write the condensed electron configuration for: a) sulphur b) silver

8. Which elements are isoelectronic with Krypton

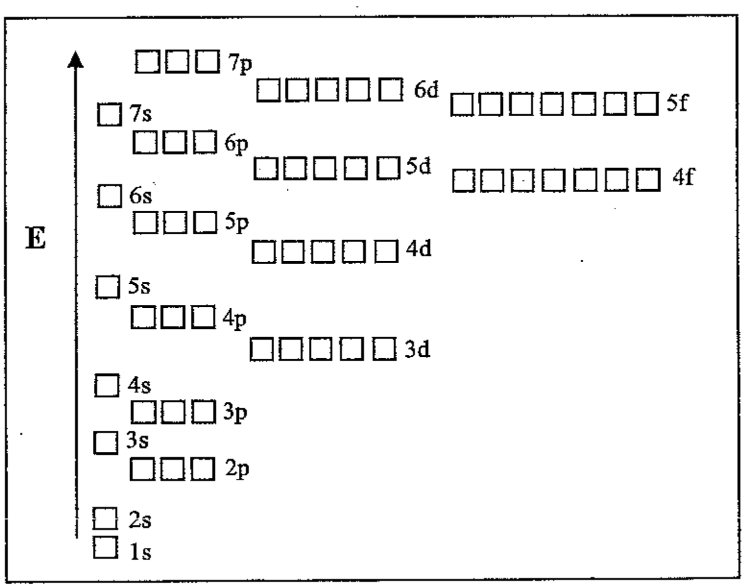
9. Write full electron configurations and orbital representations for: a) iron b) copper

10. Find three examples of transition metals that form ions using the "half full or full" rule.

11. What orbital has the quantum numbers: n=3, l = 2, m_l = 1

12. Which of the following sets of quantum numbers is not allowed? Explain.
a) n = 2, l = 1, m_l = -1, m_s = +1/2 b) n 7, l = 3, m_l 0, m_s = -1/2 c) n = 4, l = 2, m_l = 3, m_s = +1/2

Arrangement of Sublevels by Increasing Energy



ELECTRON CONFIGURATION

s -block d -block
p -block f -block

Transition Metals: (n – 1) d

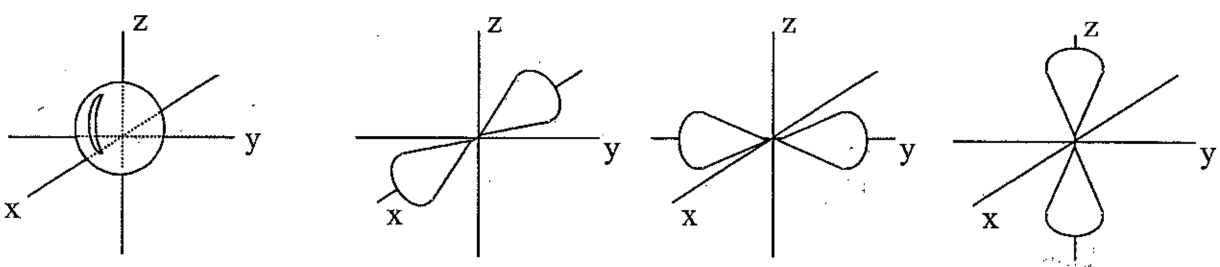
n = 1	H																	He
n = 2	Li	Be											B	C	N	O	F	Ne
n = 3	Na	Mg											Al	Si	P	S	Cl	Ar
n = 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
n = 5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
n = 6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
n = 7																		

← Metals Non-metals →

Inner Transition Metals (n – 2) f

Ce													
		U											

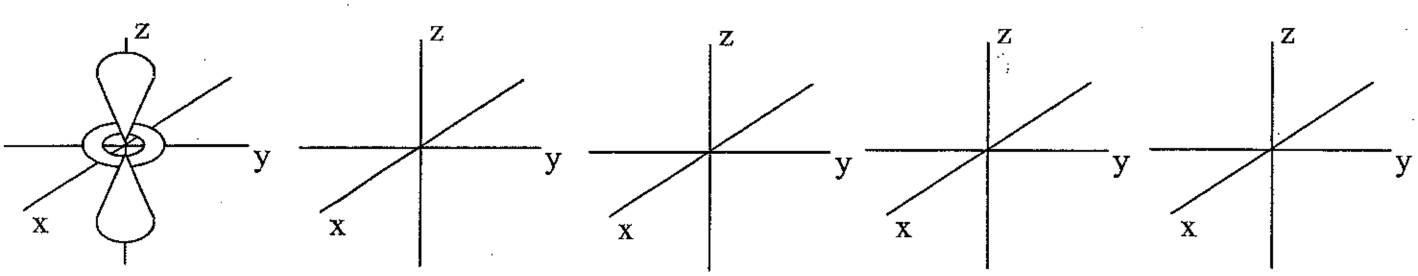
ATOMIC ORBITALS



s – orbital (spherical)

p_x p_y p_z

p – orbitals (barbell)



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

d – orbitals

Effective Nuclear Charge – attraction of valence electrons to the nucleus (less than the nuclear charge because core e- partially shield valence e- from full +ve charge of nucleus)

# of protons - # of core electons = ENC

Down a group – ENC stays the same
Across a row – ENC increases - thus attraction of valence electrons to nucleus increases this explains other periodic trends …

Atomic Radius – size of atomic radius
Down a group – A.R. increases – as the number of energy levels increases thus the v.e- are further from nucleus and less attracted to it (also, e- in other filled energy levels shield v.e- from nucleus)
Across a row – A.R. decreases – as protons are more massive than e-, they have a stronger pull on e-more protons added and stronger pull on v.e-

Ionization Energy – amount of energy required to remove an e- from an atom, the stronger the pull on the v.e- by the nucleus, the greater I.E. needed to remove it
Down a group – I.E. decreases – as nucleus has less pull on v.e-
Across a row – I.E. increases – as nucleus has stronger pull on v.e-

Electron Affinity – energy released when an atom gains an e-, the stronger the attraction b/n e- an nucleus, the more energy released
Down a group – E.A. decreases – as nucleus has less pull on v.e-
Across a row – E.A. increases – as nucleus has stronger pull on v.e-

Electronegativity – the degree of attraction that an atom has for a shared pair of e- in a chemical bond, the stronger the attraction, the higher the E.N.
Down a group – E.N. decreases – as nucleus has less pull on v.e-
Across a row – E.N. increases – as nucleus has stronger pull on v.e-

Practice

1. Classify each of the following elements as a metal or non-metal. To which group of the periodic table does each belong? How many valence electrons does each have?
   a) Na b) Mg c) S d) Br e) Ne

2. Below are a series of pairs of elements. For each pair, deduce which has the SMALLEST atomic radius and the HIGHEST ionization energy. Explain.
   a) sodium and aluminum c) sulphur and chlorine
   b) magnesium and barium d) hydrogen and helium

3. Arrange the following atoms in order of the increasing value of their 1st ionization energies. Explain. Ba Ca P S F

4. Arrange the following isoelectronic ions in terms of increasing atomic radius. Explain.
   a) N^{3-}, O^{2-}, F^- b) Na^+, Mg^{2+}, Al^{3+}

Periodic Trends Worksheet

1) Rank the following elements by increasing atomic radius: carbon, aluminum, oxygen, potassium.

2) Rank the following elements by increasing electronegativity: sulfur, oxygen, neon, aluminum.

3) What is the difference between electron affinity and ionization energy?

4) Why does fluorine have a higher ionization energy than iodine?

5) Why do elements in the same family generally have similar properties?

Practice:

1. Here are the first six ionization energies (in kJ mol^{-1}) of two elements X and Y:

5

$$X(g) \xrightarrow{1402} X^{+}(g) \xrightarrow{2855} X^{2+}(g) \xrightarrow{4522} X^{3+}(g) \xrightarrow{7452} X^{4+}(g) \xrightarrow{9462} X^{5+}(g) \xrightarrow{53170} X^{6+}(g)$$

$$Y(g) \xrightarrow{1315} Y^{+}(g) \xrightarrow{3387} Y^{2+}(g) \xrightarrow{5317} Y^{3+}(g) \xrightarrow{7452} Y^{4+}(g) \xrightarrow{11010} Y^{5+}(g) \xrightarrow{13320} Y^{6+}(g) \longrightarrow Y^{7+}$$

i. The element Y has an atomic number greater by one than that of X. What would you expect the approximate seventh ionization energy of Y to be? State briefly the reasons for your answer.

ii. The element Z has an atomic number less by one than that of X. the first four ionization energies (in kJ mol^{-1}) of Z are:

$$Z(g) \xrightarrow{1089} Z^{+}(g) \xrightarrow{2350} Z^{2+}(g) \xrightarrow{4650} Z^{3+}(g) \xrightarrow{6200} Z^{4+}(g)$$

What would you expect the approximate fifth ionization energy of Z to be? State briefly the reasons for your answer.

2. The following table shows the first three ionization energies (in kJ mol^{-1}) of elements in the same group of the Periodic Table:

Element	1st I.E	2nd I.E	3rd I.E
A	383	2437	not known
B	409	2667	3881
C	425	3065	4438
D	502	4568	6929
E	527	7314	11840

i. Which of these elements should have the largest atomic number? Give reasons for your answer.

ii. In which group of the Periodic table should the elements be placed? Give reasons for your answer.

3. The electron energy levels of a certain element can be represented by:

$$1s^2 2s^2 2p^6 3s^2 3p^1$$

Sketch a graph showing a general form which you would expect for the first five ionization energies of the element.

Use the following table to answer questions 4-7

Element	1st IE	2nd IE	3rd IE	4th IE
A	520	7301	11817	not known
B	578	1817	2746	10813
C	1087	2354	4621	6425
D	496	4566	6917	9547
E	590	1146	4944	6469

4. Which of the elements, when it reacts, is most likely to form a 3+ ion?
5. Which one of the following pairs of elements are likely to be in the same group of the Periodic Table?
   i. B and E ii. A and D iii. D and E iv. B and C v. C and E
6. Which of the elements would require the most energy to convert its atoms into ions carrying one positive charge?
7. Which of the elements would require the most energy to convert its atoms into ions carrying two positive charges?