

tutorial question and additional work

chapter 1

section 1.1-1.3

self test 1.1

self test 1.2

read 1.3d-1.3g

(see section 1.3 for explanation)

section 1.5-1.6

Self test 1.7-1.11

Exercises 1.9-1.15, 1.17-1.26, 1.28-1.31 (pp 32-33)

section one general review

Quantum numbers

Introduction

Orbitals are a spacial distribution of electron density. All energy states of electrons within atoms are negative by convention, (as they are considered to be the minimum energy necessary to free that electron from its parent atom)

principle quantum number

n

range

$$n \in \mathbb{Z}^+ | n \geq 1$$

NOTE: although n is theoretically unbounded values greater than five have not yet been observed in reality.

details

Identifies a specific energy state Orbitals of the same quantum number form an part of the same electron shell

Azimuthal quantum number (orbital angular momentum number)

l

encoding

values of l are given letters for identification

$$0 \rightarrow s$$

$$1 \rightarrow p$$

$$2 \rightarrow d$$

$$3 \rightarrow f$$

range

$$l \in \mathbb{Z} \quad | \quad 0 \leq l \leq n - 1$$

details

determines the size and shape of the sub shell/ determines the area around the nucleus which the electron may inhabit.

Magnetic quantum number

m_s

range

$$m_l \in \mathbb{Z} \quad | \quad -l \leq m_l \leq l$$

details

determines the three dimensional orientation of sub shell.

spacial orientations

P orbitals have three possible orientations

X,Y,Z

D orbitals have five possible orientations

$$xy, xz, zy, z^2, x^2 - y^2$$

F orbitals have seven possible orientations.

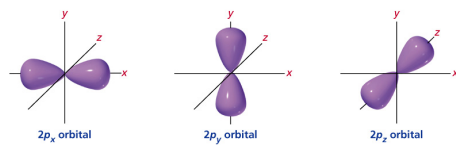
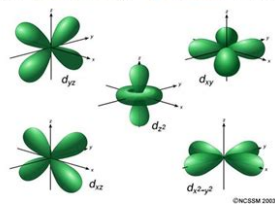


Figure 1: p orbital orientations

“d” shape (cloverleaf) – 5 orbital orientations (m)



“f” shape (indeterminate) – 7 orbital orientations (m)

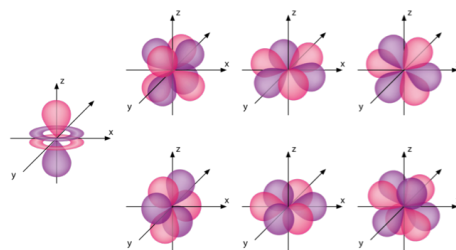


Figure 3: forbital orientations

magnetic spin number m_s

range

$$m_s \in \left(\frac{+1}{2}, \quad \frac{-1}{2} \right)$$

details

determines the direction of spin/ gyration of the electron in regard to the magnetic axis of the atom.

representation diagrams

Standard representation

$$nl^s$$

Where:

n= principle quantum number

l= azimuthal number

x= number of electrons within the l subshell.

Condensed representation

[noble gases] valence shell in standard representation

Pauli Exclusion Principles.

no two electron within one atom can have the same set of quantum numbers

Aufbau Principle

electrons must always fill into the lowest energy levels available, this provides the stable ground state for of the atom.

Hund's

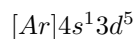
degenerate orbitals must always be filled singly and by electrons with the same spin number before 2 electrons may fill the same orbital, and opposite spin numbers are permissible.

exchange with higher sub-shells

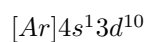
electrons are most likely to be promoted into higher sub-shells when in doing so they can lead to completely singly filled, or completely double filled orbitals.

examples

Chromium



Copper



Effective nuclear charge

effective nuclear charge is the charge exerted on a given electron within an atom by the (positively charged) nucleus of that atom

shielding

shielding is the reduction of the full nuclear charge which and in isolation the nucleus would exert on an electron.

$$Z_{eff} = Z - \sigma$$

where: Z_{eff} = effective nuclear charge Z = nuclear charge σ = shielding effect of other electrons.

this shielding effect is due to the presence of other electrons within the atom which repel the electron in question reducing the net attractive force towards the nucleus which it feels.

(this reduction is often expressed as the reduction of Z to Z_{eff})

penetration

the potential for the presence of an electron inside shells of other electrons. (?)

Slater's Rules

Estimated value for sigma

final electron is in a s or p orbital

- n-1 electrons contribute 0.85
- ns and np electrons contribute 0.35 to σ
- n-2 or lower electrons contribute 1.0 to σ

final electron is in a d or f orbital

- nf and nd electrons contribute 0.35 to σ
- electrons in lower shells contribute 1. to σ

Trends

#1

The closer to the nuclear an electron is the smaller the difference between Z and Z_{eff} will be.

#2

In terms of energy levels $d > p > s$

summary

Increases up and across the periodic table.

Exceptions

Hydrogen

the 2s and 2p orbitals have the same energy level.

potassium and calcium

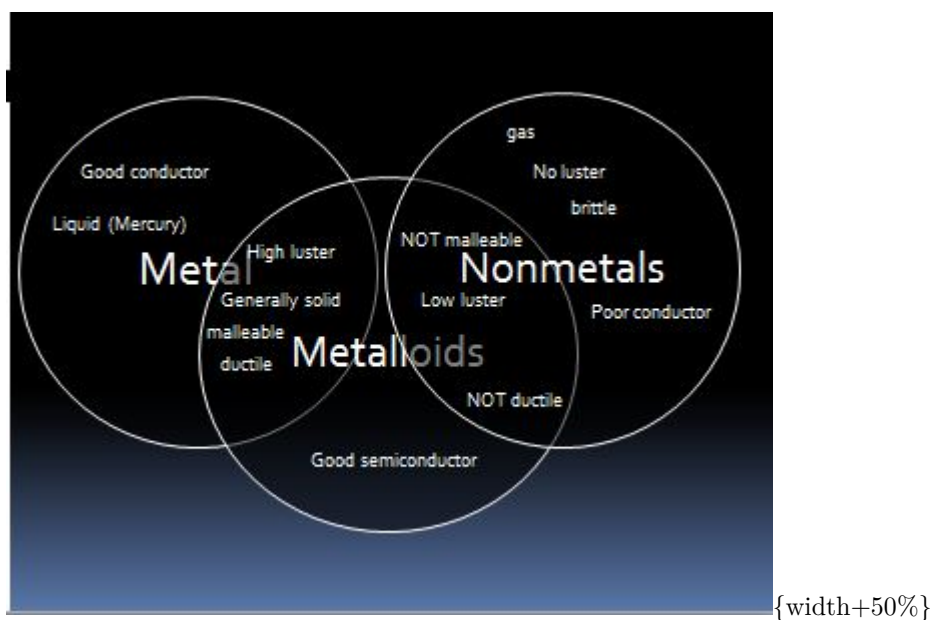
4s energy level is lower than the 3p (?) (see section 1.3 for explanation)

Periodic table

History

first proposed in 1869 based on increased atomic weight.

families of elements with similar chemical properties (groups) with gaps in these families allowing for prediction.



Atomic properties

Atomic and Ionic radii

radii measures are not very precise

Trends

increases down group and decreases across period.

this trend is offset between strontium and barium because Z_{eff} is increased as there are more protons but few effectively shielding electrons. For orbitals are very bad at shielding (?)

Lanthanoid Contractions

D block elements don't tend to expand or shrink properly

Covalent radius

half of the difference between centres of atoms in covalent bond (there is some overlap)

Ionic Radius

radius of atoms within ionic compounds, an average must be taken over many different ionic compounds as there is no reason to assume it would be half way between the atom centres.

mono atomic cations

monatomic cations are smaller than the parent atoms, as there is less shielding but equal nuclear charge so high effective nuclear charge.

monatomic anions

monatomic anions are larger than their parent ions because they experience more shielding so lower effective nuclear charge

Metallic

half of the distance between atoms in a solid.

Ionization Energy

Ionisation energy is the energy required to remove an electron from an atom (the standard is measured in gaseous conditions)

Trends

Ionisation energy increases up a group and across a period.

Correlated with atomic radii, but there are often exceptions depending on which sub-shell the electron in question is removed from.

Electron Affinity

Electron enthalpy gain $\Delta_{eg}H^\circ$

$$\Delta_{eg}H^\circ = -E_a - \frac{5}{2RT}$$

E_a is determined by the energy of the lowest unfilled or half filled orbital.

E_a can be high if the electron added can experience a strong effective nuclear charge.

Electronegativity χ

the power of an element to attract electrons towards itself when it is part of a compound.

Mulliken Electronegativity (χ_M)

Atoms with higher ionisation energies and electron affinities are more likely to gain electrons

Atoms with low ionisation energies and low electron affinities are more likely to lose electrons.

$$\chi_M = (I + E_a)$$

Pauling Electronegativity

Pauling energetics is related to the energetic of bond formation

If $BE(A-B) > \frac{1}{2}(BE(A-A) + BE(B-B))$ then the covalent bond contains an ionic contribution

Equation (?)

Trends

related to atomic size and electron configuration

increases up group and across period.

Polarizability

the ability of an atom to be distorted by an electric field

polarizable

large highly charged anions are highly polarisable.

Cations that do not have noble gas configuration are easily polarisable.

polarizing or polarizing ability.

small highly charge cations have high polarisability.

Electron structures

###Lewis structures. A covalent bond is formed when two neighbouring atoms share an electron pair.

The Octet Rule

Each atom share electrons with neighbouring atoms to achieve a total on 8 valence electrons.

(there are many exceptions to this rule.)

Procedure.

1. Count the total number of valence electrons from all atoms involved, (add/subtract for ions as necessary.)
2. Atom which is least electronegative (cannot be hydrogen)
3. Make octets around outer atoms.
4. Share as many outer electron pairs with central atom to make covalent bonds as necessary to create an octet around central atom.
5. determine which structure has the lowest overall formal charge, and the most electro-negative formal charge on the most negative atom.

Exceptions

Expanded Octets

the presence of available d orbitals within acceptable energy ranges allows for more than 8 valence electrons around the central atom. this confirmation is known as hypervalent.

Formal charge.

The number of electrons assigned to each atom. is The sum of its unshared valence electrons plus 1 electron per covalent bond it forms

the formal charge of an atom in a compound is the number of electrons normally present in its valence shell minus the number of electron assigned to it in its given lewis structure.

NOTE: Sometimes lowest formal charge violates octet rule for central atom

Resonance

when two, or more lewis structure with identical formal charges and atomic conformation indicates a resonance structure. this compound exist in a state between the two formal structures, with intermediate bond lengths and energy levels. As bonding is distributed across the whole molecule so the energy of the resonance hybrid is lower than any single structure

Predicting Shapes

Bonding vs Non Bonding pairs.

non bonding electrons have a greater repellent force, hence their position equatorial/ axial must place them as far away from each other as possible, and as far away from as many other electrons pairs as possible.

Bonding pair are also physically smaller than non bonding pairs.

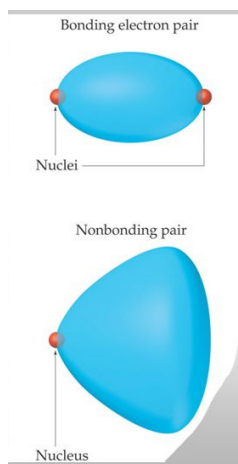


Figure 5: Bonding vs Non Bonding Pairs

Bond Angles

Exceptions

1. Lone pairs distort bond angles by about 2.5 degrees
2. multiple bonds also distort bond angles.

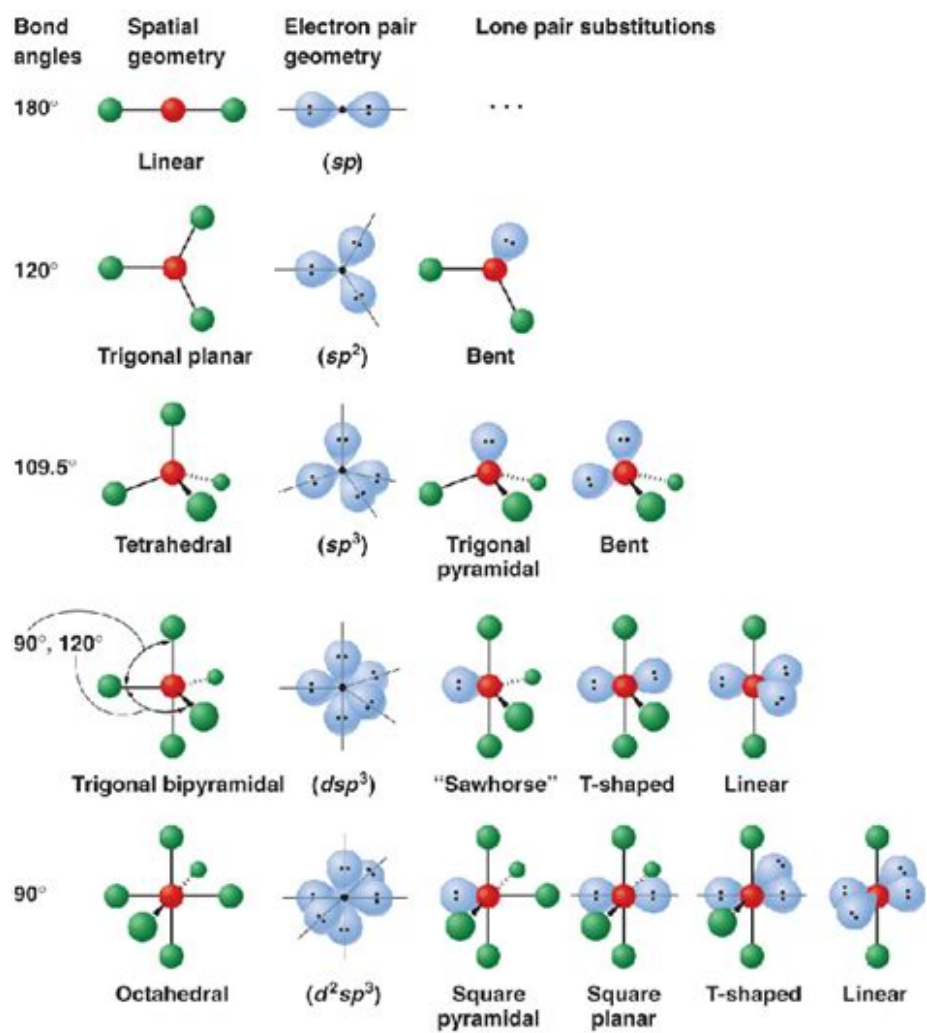
*d

Electron regions (steric number)	Electronic geometry	Bond angles
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°
5	trigonal bipyramidal	90°, 120°, and 180°
6	octahedral	90° and 180°

Figure 6: Bond Angles

Number Of Electron Dense areas	Electron Pair Geometry	No Lone Pairs	1 lone Pair	2 Lone Pairs	3 Lone Pairs
2	Linear	Linear			
3	Trigonal Planar	Trigonal Planar	Bent		
4	Tetrahedral	Tetrahedral	Trigonal bipyramidal	Bent	
5	Trigonal bipyramidal	Trigonal Bipyramidal	Sawhorse	T- Shaped	Linear
6	Octahedral	Octahedral	Square Pyramidal	Square Planar	T- Shaped

This table is fucked, it will not display for shit*



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Figure 7: ElectronDomainGeometry