

UNIT II ATOMIC STRUCTURE

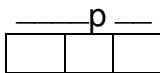
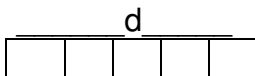
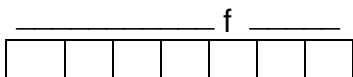
I. The Bohr's Model:

2. Electron Configuration of Atoms (Multi-electron Systems):

Maximum number of electrons that can occupy an energy level = $2n^2$

potential energy	$n=\infty$	
	$n=4$	_____ 32 e ⁻
increases	$n=3$	_____ 18e ⁻
	$n=2$	_____ 8 e ⁻
	$n=1$	_____ 2 e ⁻

Sublevels: The **s**-, **p**-, **d**-, and **f**-**sublevels** have **one**-, **three**-, **five**-, and **seven** **-orbitals** respectively. . Each orbital may be occupied by no more than **two electrons**. Therefore, a filled s-, p-, d-, and f- sublevels may be designated as **s²**, **p⁶**, **d¹⁰**, and **f¹⁴** respectively.



a) Triangular Array:

1s			
2s	2p		
3s	3p	3d	
4s	4p	4d	4f
5s	5p	5d	5f
6s	6p	6d	
7s	7p		
8s			

Exercise: Write the electron configuration for :

i) Co (Z=27)

ii) S (Z= 16)

iii) Ca (Z= 20)

b) Periodic Chart:

1 s		1 s
2 s		2 p
3 s		3 p
4 s	3 d	4 p
5 s	4 d	5 p
6 s	5 d	6 p
7 s	6 d	7 p
4 f		
5 f		

Exercise: Write the electron configuration for the atoms given below in a **short notation form**.

i) Co ($Z=27$)

ii) S ($Z= 16$)

iii) Ca ($Z= 20$)

3. The Electron Configuration of Ions:

Write the electron configuration for Co^{2+} :

4. Energy Level Diagram for a One-electron System:

5. Quantum Mechanical Model (Wave mechanics, Quantum mechanics) for the atom.

Orbit (in terms of Bohr's model) versus orbital (in terms of wave-mechanics):

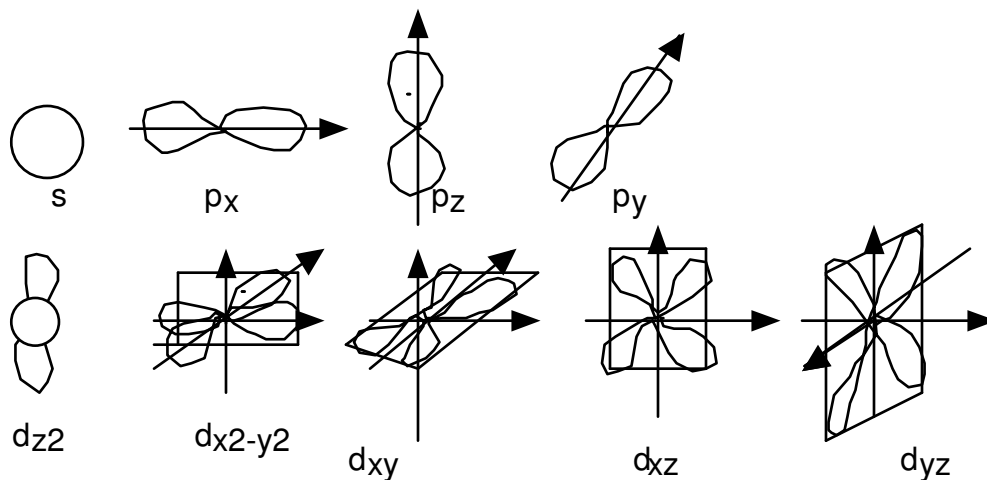


Figure:Contour diagrams of the s-, p-, and d-orbitals

6. The Four Quantum Numbers: The first three quantum numbers result from the solutions of the wave equation(a mathematical equation), Shroedinger equation. The fourth quantum number, S , was found experimentally.

a) The principal quantum number,n:

- Can only have positive integral values: 1,2,3,4,.....,∞ .
- Is related to the average distance of the electron from the nucleus (main energy level).

b) Azimuthal Quantum Number (Orbital angular Momentum Quantum Number),l:

(subsidiary energy level)

- Can only have integral values.
- Range: 0, 1, 2, , (n-1).
- Related to shape of an orbital.
- Letter designations:

l	designation
0	s
1	p
2	d
3	f
4	g

c) Magnetic Quantum Number, m: (m_l or m)

- For a given l , value can vary between the limits of $+l$ to $-l$.
- Total m values are: $2l + 1$.
- Roughly characterizes the directions of maximum extension in space of the electron cloud. (Or, roughly related to the way an electron cloud orients in a magnetic field).

Variation of m with l :

d) Spin Quantum Number (M_s or S) :

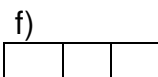
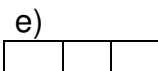
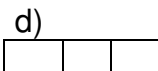
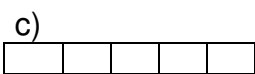
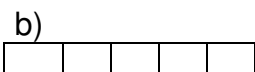
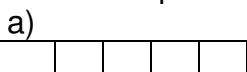
- Characterizes the spin of the electron on its own axis.
- May have value of either $+1/2$ or $-1/2$

The Pauli Exclusion Principal: *No two electrons in any one atom may have all four quantum numbers the same.* In effect, this limits the number of electrons in any given orbital to two, and it also requires that the spins of these two electrons be in opposite directions.

Hund's Rule (maximum unpaired parallel spin): *Electrons entering a subshell containing more than one orbital will be spread out over the available orbitals with their spins in the same direction.*

Exercise:

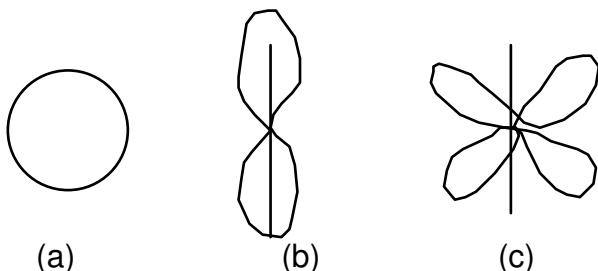
1) Which of the following box diagrams for the electron distribution is unacceptable as a stable state (ground state) ? Why ?



2) Which of the following represents an unreasonable set of quantum numbers ?

	n	l	m	S
a)	5	- 2	+ 1	+ 1/2
b)	3	3	- 2	+ 1/2
c)	2	0	0	- 1/2
d)	5	3	- 3	+ 1

3) Consider the atomic orbitals, (a,b,c), shown below:



i) What is the number of electrons that can be contained in atomic orbital, c ?

Ans : _____

ii) How many orbitals with the same value of “m” as orbital (a) can be found in the principal energy level with $n = 4$? Ans: _____

iii) What is the smallest “n” value possible for an electron in an orbital of type (c) above ? Ans: _____

iv) What is the “l” value that characterizes orbital (a) ? Ans: _____

v) In a multi-electron system, arrange the above orbitals in order of increasing energy in the $n = 3$ shell.

Ans: _____

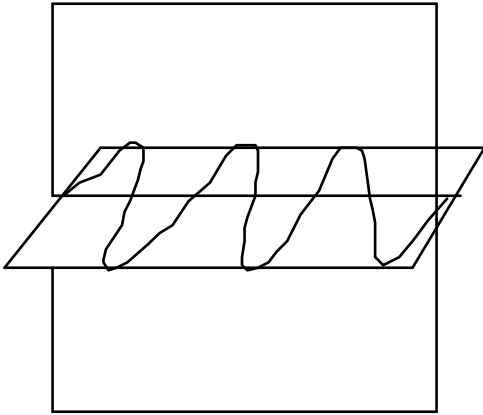
vi) How many orbitals exist , with the same value of “m” as orbital (a) , in the third shell ? Ans: _____

7) Paramagnetic Versus Diamagnetic:

Materials that are **diamagnetic** experience no attraction for another magnet. In these substances there are the same number of electrons of each spin, so their magnetic effects cancel. **Paramagnetic** substances on the other hand, are weakly attracted to a magnetic field. In these materials there are more electrons of one spin than other and total cancellation does not occur. The extra electrons of one spin cause the atom or the molecule as a whole to behave as if it were itself a tiny magnet.

8) Electromagnetic Radiation

In 1873, Maxwell showed on theoretical grounds that visible light consists of electromagnetic waves. The electromagnetic wave has an electric component and a magnetic component perpendicular to it. Maxwell's theory provided a mathematical description for the general behavior of light. Light energy (radiation) propagated in space in the form of vibrating electric and magnetic fields.



The Nature of Radiation:

Light is an electromagnetic wave. It has a wave-like property. A wave can be thought of as a vibrating disturbances by which energy is transmitted.

The wavelength, λ , is the distance between identical points on successive waves. The unit of λ is _____.

The frequency, ν , is the number of cycles of a moving wave that passes a given point/time. The unit is _____.

The relationship between λ and ν :

$$\lambda \cdot \nu = c$$

c =speed of light= 3.00×10^{10} cm/sec

Various Types of Electromagnetic Radiation: These differ only in λ and ν . They are alike in other respects.

radio wave	micro wave	infrared	visible	ultra violet	x-ray	ray
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Higher frequency
Higher energy \longrightarrow

The higher the ν , the more energetic the radiation.

$$E \propto \nu$$

Planck's Quantum Theory (1900)

According to classical physics the radiant energy emitted by a solid could have an energy value within a continuous range. Scientists could not explain the dependence of emitted radiation on the wavelength, λ . According to Planck's quantum theory, radiant energy could not have any arbitrary value; instead, the energy could only be emitted in small discrete amounts he called "quanta" or "photon".

$$E_{\text{radiation}} = h \nu$$

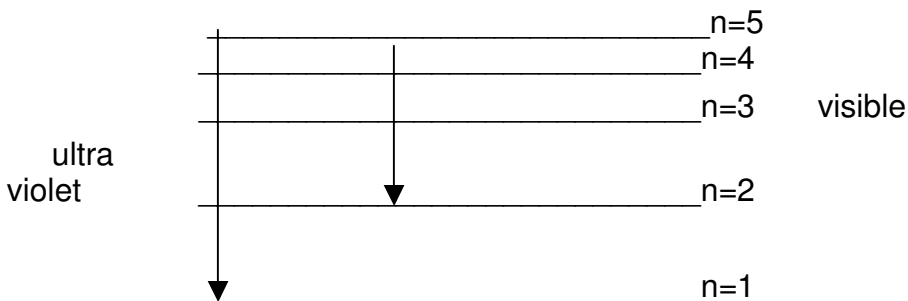
"h" is Planck's constant and is equal to 6.63×10^{-27} erg.sec or 6.63×10^{-34} joule.sec.

11. The Bohr Atom

Bohr applied the quantum theory to the atomic hypothesis. He developed a model of the hydrogen atom which allowed him to explain the frequencies of the emitted radiation. His reasoning involved the following postulates:

- The electron moves in a circular orbit around the nucleus.
- The electron in an atom has only certain definite stationary states allowed to it. Each of these stationary states has a definite fixed energy.

$$E_n = - \text{constant} \frac{1}{n^2} \cdot Z^2$$



- When an atom is in one of these states it does not radiate. But, when changing from a high energy state to a lower energy, the atom emits radiation. The energy of radiation is equal to the difference in the energy of the two states.

$$\text{Eradiation } = \Delta E = E_{(2)} - E_{(1)} = h \nu = + \text{constant} \left[\frac{1}{n_{(1)}^2} - \frac{1}{n_{(2)}^2} \right] Z^2$$

$$\frac{1}{\lambda} = + \frac{\text{constant}}{h.c} \left[\frac{1}{n_{(1)}^2} - \frac{1}{n_{(2)}^2} \right] Z^2$$

$$\frac{1}{\lambda} = + R \left[\frac{1}{n_{(1)}^2} - \frac{1}{n_{(2)}^2} \right] Z^2$$

R=Rydberg constant= 109677 cm^{-1} and $n_{(2)} > n_{(1)}$

Bohr was able to explain the origin of emission spectrum of the Hydrogen atom. He predicted the values of some frequencies of light waves. He was able to explain why only certain frequencies of light were radiated by atoms. He explained it as due to certain transitions of the electron atom from specific energy levels to others.

Exercise:

Calculate the energy, in electronvolts, of the photon whose wavelength is 6563 \AA ($1 \text{ ev} = 1.60 \times 10^{-12} \text{ erg}$, $h = 6.63 \times 10^{-27} \text{ erg.sec}$, $1 \text{ cm} = 10^8 \text{ \AA}$)

Setup:

Answer: 1.89 ev

Exercise:

Calculate the wavelength of the line in the hydrogen spectrum which appears when an excited hydrogen drops from the fourth to the second energy level (Balmer series). Rydberg constant, $R = 109678 \text{ cm}^{-1}$.

Setup:

Exercise:

The wavelength of a spectral line of the hydrogen atom is 95.0 nm.

a) What is the frequency of the light wave? (1 meter= 10⁹ nm).

Setup:

Answer: 3.16 x 10¹⁵ Hz

b) What is the energy of the light wave?

Setup:

Answer: 2.09 x10⁻¹⁸ joules

12. De-Broglie (1924) Dual Nature of Light (Wave-like and Particle-like)

De Broglie suggested that if light can behave in some instances as if it were composed of particles, perhaps particles, at times, exhibit properties that we normally associate with waves.

Einstein had shown that the energy equivalent, E, of a **particle** of mass ,m, is equal to:

$$E= m c^2 \quad (\text{Where } c \text{ is the speed of light})$$

Planck had shown that the energy of a photon (**wave**) is given by:

$$E= h \nu = \frac{h c}{\lambda}$$

Equating the above,

$$= \frac{h}{m.c}$$

If this equation applies to a particle, such as the electron, the equation can be written as:

$$= \frac{h}{mv}$$

[Here we replaced " c " (the speed of light) by "v " (the speed of the particle).] Hence, the electron has dual nature, a wave-like and a particle-like, just as the photon.

λ is the wavelength associated with the particle of mass, m, and velocity, v .

Exercise:

If the electron is found to be moving at a speed of 2.6×10^9 cm/sec, calculate the associated wavelength.

(1 erg= g.cm²/sec² , mass of 1 electron = 9.1×10^{-28} g)

Setup:

Answer: 0.28 °A

Exercise:

What is the wave length of a grain of sand that weighs 1.0×10^{-5} g and is moving at a speed of 0.010 m/sec (approximately 0.02 mile/hr) ?

Setup:

Answer: 6.6×10^{-24} m

13. Heisenberg Uncertainty Principle:

If one attempts to look at an electron, the effect of impinging photons would be to change its position and momentum. Lowering the energy of the photon reduces the resolution possible and increases the uncertainty of its position. On the other hand, increasing the energy improves the resolution and increases the uncertainty in momentum !

We cannot know the position and momentum of a particle precisely. The more precisely we determine one, the more uncertain we must be of the other. The product of uncertainty is comparable in magnitude to Planck's constant, h.

$$\Delta mv \cdot \Delta x \geq \frac{h}{4 \pi}$$

Electron-Dot Structure and molecular Geometry

1. Review the Rules for Drawing Lewis (Electron-Dot) Structure

- i. Count all the valence electrons of the atoms. (If the species is an ion, add an additional electron for each negative charge or subtract an electron for each positive charge.)
- ii. Place one pair of electrons for each bond.
- iii. Complete the octets of the atoms bonded to the central atom. (Remember that the valence shell of any hydrogen atom is complete with only two electrons.)
- iv. Place any additional electrons on the central atom **in pairs**.
- v. If the central atom still has less than an octet, you must form multiple bonds so that each atom has an octet.

2. Exceptions to the Octet Rule:

- a. Electron deficient molecules: This is typical of molecules where the central atom belongs to group IIIA.

Example: BCl_3

- b. Expanded valence shell: This is typical of molecules where the central atom belongs to the 3rd, 4th, 5th, or 7th period.

Example: SF_6

- c. Odd molecules: (These are molecules that have an odd number of valence electrons.)

Example: NO_2

3. Practice Drawing Lewis Structures:

a) SCl_4

b) SO_2

c) NH_4^+	d) ICl_4^-
e) ClF_3	f) NO_3^-
g) CO_3^{2-}	h) CO_2
i) HCN	j) XeF_4

4. The Valence Shell Electron Pair Repulsion Theory,(VSEPR Theory).

The electron pairs present in the valence shell of the central atom tend to stay as far as possible to minimize repulsion.

Arrangement of Electron pairs:

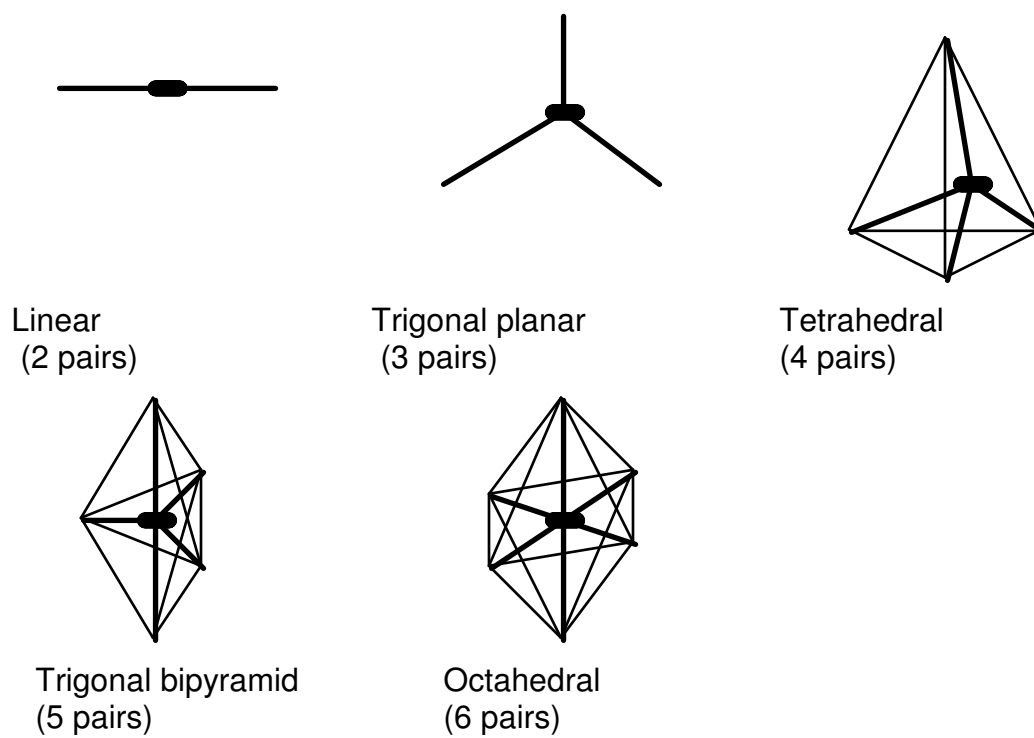


Figure: arrangement of electron pairs to minimize repulsion.

No of electron pairs	shape (geometry of electron pairs)	Example	Bond Angle
2	Linear	BeCl ₂	180°
3	Trigonal planar (triangular planar)	BCl ₃	120°
4	Tetrahedral	CH ₄	109°
5	Trigonal Bipyramid	PCl ₅	90° and 120°
6	Octahedral	SF ₆	90°

5. The Geometric Arrangement of Electron Pairs Dictates the Geometry of the Molecules or Ions

I) Shapes derived from a **triangular planar** arrangement of electrons.
Shape of molecule

Examples: SO_2 , and NO_2^-

II) Shapes derived from a **tetrahedral** arrangement of electrons.

a) Examples: NH_3 , ClO_3^- , SO_3^{2-} , PCl_3 , and H_3O^+ .

b) Examples: H_2O , and ClO_2^- .

III) Shapes derived from a **trigonal bipyramid** arrangement of electrons.

a) Examples: SF_4 , TeCl_4 , and IF_4^+ ,

b) Example: ClF_3

c) Example: XeF₂ and I₃⁻

IV) Shapes derived from **octahedral** arrangement of electrons.

a) Example: BrF₅, SbCl₅²⁻ and XeOF₄

b) Example: XeF₄, and ICl₄⁻

6) The VSEPR Model and the Multiple Bond:

A multiple bond (a double or a triple bond) should be counted as one effective pair in using VSEPR model. The multiple bond acts as one center of electron density.

Examples: SO₂, CO₂, CO₃²⁻, and NO₃⁻

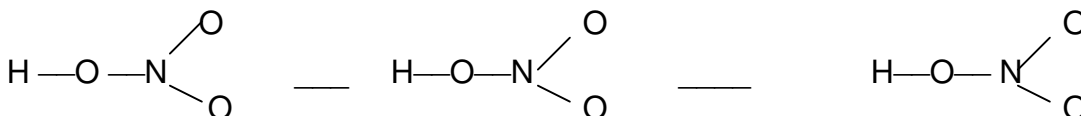
SUMMARY: Predicting the geometry of small molecules and polyatomic ions using the VSEPR theory:

- Write the Lewis (Electron-dot) structure.
- Consider only the electrons around the central atom.
- Determine the geometry of the **“groups” of electrons**.
- Determine the geometry of the **molecule** or ion.
- Make the following addition to the original postulate of the VSEPR model:
Lone pairs require more room than **bonding pairs** and tend to compress the angles between the bonding pairs. (In a bonding pair of electrons, the electrons are shared by two nuclei. In a lone pair, both electrons must be close to a single nucleus and tend to take more of the space around that atom.)

Lone pair-lone pair repulsion > Lone pair-bond pair repulsion > Bond pair-bond pair repulsion.
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7) Formal Charges and Resonance Structures

All resonance forms for a given molecule or ion must have the same configuration of nuclei. The resonance forms of a given species differ in the arrangement of electrons not in the arrangement of nuclei.



To evaluate the resonance forms that contribute most to the actual structure of the molecule or ion we need to consider the formal charges and a set of rules. A **formal charge** of an atom in a Lewis formula is a hypothetical charge that we obtain by dividing the bonding electrons **equally** between the bonded atoms, and then comparing the number of electrons that a given atom has in the structure with the number of valence electrons that this atom would have when electrically neutral.

In a molecule, the sum of the formal charges is zero. In an ion, the formal charges add up to the charge of the ion.

Rules:

a) Atoms that are bonded to each other in a structure should not have formal charges with the **same sign**. A Lewis structure in which the adjacent charge rule is violated will contribute less to the actual structure.

b) The most important resonance forms should have the **smallest number of formal charges** and the **lowest magnitudes of these charges**. The best forms would have no formal charges at all.

c) The most important resonance forms would have a distribution of positive and negative formal charges which are in agreement with the electronegativity of the atoms. That is, the most electronegative atom in the molecule should not have a positive formal charge.

Exercise:

Draw all resonance forms for the OCN^- ion. Decide which form would contribute the least to the actual structure of the ion.

