Chemical Bonding: Time Economic Innovative Pedagogies - A Review Article

By Arijit Das

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Keywords: chemical education research, engineering UG level students, chemical bonding, hybridization & geometry, molecular orbital theory, bond order, oxide based acid radical, magnetic properties, spin multiplicity, chemical bonds, alkenes and alkynes.

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CHEMICALBONDINGTIMEECONOMICINNOVATIVEPEDAGOGIESAREVIEWARTICLE

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I. INTRODUCTION

The conventional methods[1-7] for determination of hybridization of simple molecules or ions, bond order of diatomic species having $(1\text{-}20)e^-s$ using M.O.T., bond-order of oxide based acid radicals, prediction of spin state using spin multiplicity value, evaluation of magnetic behaviour of diatomic species having $(1\text{-}20)e^-s$ with M.O.T., calculation of number bonds in olefinic hydrocarbons and alkynes are time consuming. Keeping this in mind, in this survey, I have introduced some innovative teaching methodologies[8-18] to make chemistry fascinating and time economic. Here, I have tried to discuss them abruptly with different multiple choice questions.

II. TIME ECONOMIC INNOVATIVE PEDAGOGIES

a) Predicting the Hybridization of Simple Molecules/ions

In chemistry, hybridization is the concept of mixing atomic orbitals into newly hybrid orbitals suitable for the pairing of electrons to form chemical bonds in valence bond theory (VBT). Hybrid orbitals are differ in energies, shapes, etc., than the component atomic orbitals. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties. Prof. Linus Pauling (1931), first proposed the Hybridization in order to explain the structure of molecules such as methane (CH_4) using atomic orbitals. Here, an innovative time economic methodology proposed for the determination of hybridization state .

i. Prediction of sp, sp^2, sp^3 Hybridization state

Hybridization is nothing but the mixing of orbital's in different ratio and the newly mixed orbitals called hybrid orbitals. The mixing pattern is as follows:

s + p (1:1) - sp hybrid orbital;

s + p (1:2) - sp^2 hybrid orbital;

s + p (1:3) - sp^3 hybrid orbital

Formula used for the determination of sp, sp^2 and sp^3 hybridization state:

Power on the Hybridization state of the central atom = (Total no of σ bonds around each central atom -1)

All single (-) bonds are σ bond, in double bond (=) there is one σ and 1π, in triple bond (≡) there is one σ and 2π. In addition to these each lone pair (LP) and Co-ordinate bond can be treated as one σ bond subsequently.

Eg.:

1. *In NH_3:* central atom N is surrounded by three N-H single bonds i.e. three sigma (σ) bonds and one lone pair (LP) i.e. one additional σ bond. So, in NH_3 there is a total of four σ bonds [3 bond pairs (BPs) + 1 lone pair (LP)] around central atom N. Therefore, in this case power of the hybridization state of N = 4-1 = 3 i.e. hybridization state = sp^3.

2. *In H_2O:* central atom O is surrounded by two O-H single bonds i.e. two sigma (σ) bonds and two lone pairs i.e. two additional σ bonds. So, altogether in H_2O there are four σ bonds (2 bond pairs + 2 lone pairs) around central atom O, So, in this case power of the hybridization state of O = 4-1 =3 i.e. hybridization state of O in H_2O = sp^3.

3. *In H_3BO_3:* B has 3σ bonds (3BPs but no LPs) and oxygen has 4σ bonds (2BPs & 2LPs) so, in this case power of the hybridization state of B = 3-1 = 2 i.e. B is sp^2 hybridized in H_3BO_3. On the other hand, power of the hybridization state of O = 4-1= 3 i.e. hybridization state of O in H_3BO_3 is sp^3.

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$$\overset{\displaystyle :}{\underset{\displaystyle}{:O-H}}$$

$$\overset{\displaystyle |}{B}$$

$$H-\overset{..}{\underset{..}{O}}\qquad\overset{..}{\underset{..}{O}}-H$$
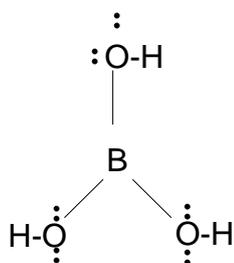
4. *In I-Cl:* I and Cl both have 4σ bonds and 3LPs, so, in this case power of the hybridization state of both I and Cl = 4 - 1 = 3 i.e. hybridization state of I and Cl both are sp^3.

5. *In* $CH_2=CH_2$: each carbon is attached with 2 C-H single bonds (2 σ bonds) and one C=C bond (1σ bond), so, altogether there are 3 sigma bonds. So, in this case, power of the hybridization state of both C = 3-1 = 2 i.e. hybridization state of both C's are sp^2.

$$\underset{\displaystyle H \qquad\qquad H}{\overset{\displaystyle H \qquad\qquad H}{C=C}}$$
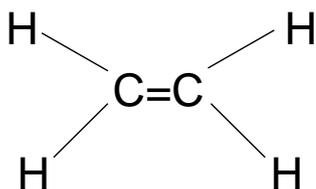
b) *Prediction of* sp^3d, sp^3d^2, sp^3d^3 *Hybridization state*

In case of sp^3d, sp^3d^2 and sp^3d^3 hybridization state there is a common term sp^3 for which 4 sigma bonds are responsible. So, in addition to 4 sigma bonds, for each additional sigma, added one d orbital gradually as follows:-

5σ bonds = 4σ bonds + 1 additional σ bond = sp^3d hybridization

6σ bonds = 4σ bonds + 2 additional σ bonds = sp^3d^2 hybridization
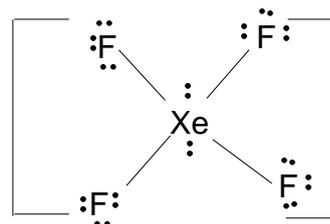
7σ bonds = 4σ bonds + 3 additional σ bonds = sp^3d^3 hybridization

Eg:-

1. IF_4^+: I has 7 e⁻s in its outermost shell, so, in this case, subtract one e⁻ from 7 i.e. 7 – 1 = 6. So, out of 6 electrons, 4 electrons form 4 I-F bonds i.e. 4 sigma bonds and there is one LP. So, altogether there are 5 σ bonds. So, 5σ bonds = 4 σ bonds + 1 additional σ bond = sp^3d hybridization".
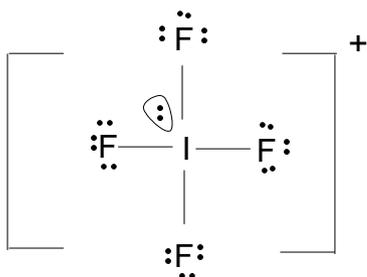
2. IF_7: 7 I-F single bonds i.e. 7σ bonds = 4σ bonds + 3 additional σ bonds = sp^3d^3 hybridization.

3. ICl_2^-: I has 7 e⁻s in its outermost shell, so, in this case, add one e⁻ with 7(overall charge on the compound) i.e. 07+1= 08. So, out of 08 electrons, 02 electrons form 02 I-Cl bonds i.e. 02 sigma bonds and there is 03 LPs. So, altogether there are 05σ bonds. So, 5σ bonds = 04 σ bonds + 01 additional σ bond = sp^3d hybridization.

4. XeF_4: Xe, an inert gas, consider 8 e⁻s in its outermost shell, 04 of which form 04 Xe-F sigma bonds and there is two LPs, i.e. altogether there is 06 σ bonds = 04 σ bonds + 02 additional σ bonds = sp^3d^2 hybridization.

$$\begin{array}{ccc}
:\!\overset{..}{\underset{..}{F}} & & \overset{..}{\underset{..}{F}}\!: \\
& \overset{..}{\underset{..}{Xe}} & \\
:\!\overset{..}{\underset{..}{F}} & & \overset{..}{\underset{..}{F}}\!:
\end{array}$$

In case of determination of the hybridization state by using the above method, one must have a clear idea about the outermost electrons of different family members in the periodic table as follows:

Family	Outermost electrons
Carbon family	04
Nitrogen family	05
Oxygen family	06
Halogen family	07
Inert gas family	08

In case of cationic species, requisite electron/electrons must be removed from the outermost orbit of the central atom and incase of anionic species, added requisite electron with the outermost electrons of the central atom. Examples have been explored in Table-1.

$$\left[\begin{array}{ccc}
& :\!\overset{..}{\underset{..}{F}}\!: & \\
:\!\overset{..}{\underset{..}{F}}\!— & \overset{(:)}{\underset{|}{I}} —\overset{..}{\underset{..}{F}}\!: & \\
& :\!\overset{..}{\underset{..}{F}}\!: &
\end{array}\right]^{+}$$

Table 1: (σ bonds and corresponding hybridization State)

Total number of sigma (σ) bonds	Nature of Hybridization State	Examples
2	sp	$BeCl_2$, $HgCl_2$, C_2H_2, CO_2, CO, $CdCl_2$, $ZnCl_2$ etc.
3	sp^2	BCl_3, $AlCl_3$, C_2H_4, C_6H_6, SO_2, SO_3, HNO_3, H_2CO_3, $SnCl_2$, $PbCl_2$ etc.
4	sp^3	NH_4^+, BF_4^-, H_2S, H_2SO_4, $HClO_4$, PCl_3, NCl_3, $AsCl_3$, $HClO_3$, ICl_2^+, OF_2, $HClO_2$, SCl_2, $HClO$, ICl, XeO_3 etc.
5	sp^3d	PCl_5, $SbCl_5$, SF_4, ClF_3, BrF_3, XeF_2, ICl_2^- etc.
6	sp^3d^2	SF_6, AlF_6^{3-}, SiF_6^{2-}, PF_6^-, IF_5, BrF_5, $XeOF_4$, XeF_4, BrF_4^-, ICl_4^- etc.
7	sp^3d^3	IF_7, XeF_6 etc.

Geometry of simple molecules or ions:

In absence of lone pair of electrons a molecule or ion exhibit regular geometry. For sp, sp^2, sp^3, sp^3d, sp^3d^2 and sp^3d^3 hybridization state, geometry will be linear, trigonal planar, tetrahedral, trigonal bipyramid, octahedral and pentagonal bipyramid respectively, where as for the same hybridization state in presence of lone pair of electrons they exhibit sub normal geometry (Fig-1, Table-2).

*Table 2:* Hybridization, Molecular Geometry and Bond Angles without/with lone pair of electrons

Hybridization	LP	Molecular Geometry (Regular/Normal)	Approximate Bond Angles (Degree)	Examples	LP	Molecular Geometry (Sub-normal)	Approximate Bond Angles (Degree)	Example
sp	0	Linear	180	CO_2, CS_2, $BeCl_2$, $HgCl_2$	-	-	-	-
sp^2	0	Trigonal Planar or Triangular planar	120	BH_3, $AlCl_3$, C_2H_4, BCl_3, BF_3, NO_3^-, CO_3^{2-}	01	Angular or V-shape	<120	SO_2, NO_2^-
sp^3	0	Tetrahedral	109.5	BH_4^-, BF_4^-, $SnCl_4$, H_2SO_4 $HClO_4$, $SiCl_4$	01	Pyramidal	<109.5	NH_3, PH_3, AsH_3
					02	Bent shape or V-shape	<109.5	H_2O, H_2S, H_2Se
					03	Linear	180	ICl, BrF, ClF
sp^3d	0	Trigonal bipyramid	120 (equatorial) 90 (axial)	PF_5, PCl_5	01	See-Saw	<120(equatorial) <90 (axial)	SF_4
					02	T-shape	<90	ICl_3, F_3Cl
					03	Linear	180	XeF_2, I_3^-
sp^3d^2	0	Octahedral	90	SF_6, WF_6, SeF_6, $SnCl_6^{2-}$	01	Square pyramidal	<90	IF_5, BrF_5
					02	Square planar	90	XeF_4
sp^3d^3	0	Pentagonal bipyramid	72 & 90	IF_7	01	Pentagonal Pyramidal or Distorted octahedral	72 & 90	XeF_6

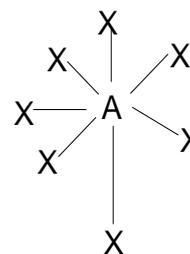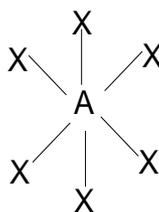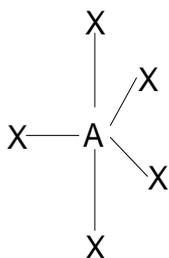*Regular/Normal Molecular Geometry without Lone pair of electrons:*

X-A-X
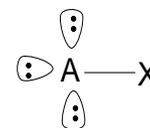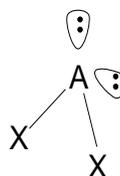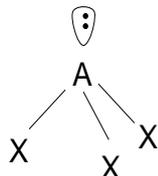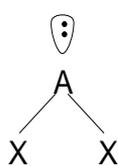(Linear, sp, LP=0)
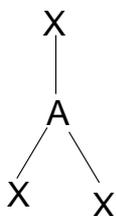
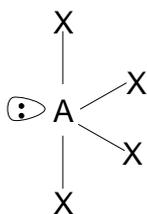(Trigonal planar, sp^2 , LP=0)
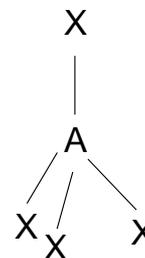
(Tetrahedral, sp^3, LP=0)

(Trigonal bipyramidal, sp^3d, LP=0) (Octahedral, sp^3d^2, LP=0) (Petntagonal bipyramidal, sp^3d^3, LP =0)
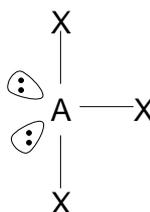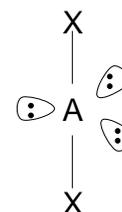
Sub-normal Molecular Geometry with Lone pair of electrons:

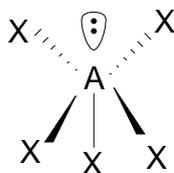(Bent or V shape, sp^2, LP = 01) (Pyramidal, sp^3, LP=01)(Bent or V shape, sp^3, LP=02) (Linear, sp^3, LP=03)
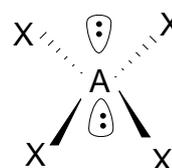
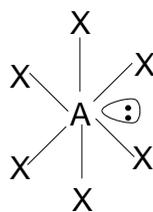(See Saw, sp^3d, LP=01)   (T shape, sp^3d, LP=02)   (Linear, sp^3d, LP=03)

(Square Pyramidal, sp^3d^2, LP=01)   (Square planar, sp^3d^2, LP=02)

(Pentagonal Pyramidal, sp^3d^3, LP=01)

Fig. 1: Pictorial diagram of molecular geometry

Problems on Hybridization and Geometry:

Q.1. In allene, hybridization of central and terminal carbons, respectively, are
   a. sp and sp^2 b. sp^2 and sp^2 c. sp and sp^3 d. sp^2 and sp^3

Ans: a. sp and sp^2 (Allene $H_2C=C=CH_2$)
                             sp^2 sp sp^2

Q.2. The species which has a square planar structure is
   a. SF_4 b. BF_4^- c. XeF_2 d. XeF_4
Ans: d. XeF_4 (Hybridization sp^3d^2, LP = 02, square planar geometry)

Q.3. The hybrid bond orbitals used by chlorine in forming ClF_3 are of the type
   a. sp^3 b. sp^2 c. sp^3d d. sp^3d^2
Ans: c. sp^3d (In ClF_3 - 5σ bonds around Cl atom.
      So, 5σ bonds = 4 σ bonds + 1 additional σ bond = sp^3d hybridization)

Q.4. Which are the species in which sulphur undergoes sp^3 hybridization ?
   A. SF_4 B. SCl_2 C. SO_4^{2-} D. H_2S
   a. A and C   b. B, C and D   c. A, B and D   d. C and D
Ans: b. B, C and D (SF_4 - 5σ bonds around S atom sp^3d hybridization)

Q.5. Which of the following compounds show linear geometry ?
   a. BeH_2 b. CH_4 c. XeF_2 d. H_2O
Ans: a. & c. (BeH_2 – hybridization sp, LP = 0, regular shape - Linear ; XeF_2 - hybridization sp^3d,
      LP = 03, sub-normal shape – Linear)

Q.6.Which of the following compound will show square pyramidal structure ?
   a. XeF_4 b. IF_5 c. IF_7 d. XeF_6
Ans: b. IF_5 (6σ bonds around I atom sp^3d^2 hybridization, LP = 01, square pyramidal geometry)

III.   PREDICTING THE BOND-ORDER OF DIATOMIC SPECIES WITHOUT MOLECULAR ORBITAL THEORY(MOT)

Bond-order usually predicted from the Molecular Orbital Theory. Molecular Orbital Theory (M.O.T.) was first proposed by Friedrich Hund and Robert Mulliken in 1933. They developed an approach to covalent bond formation which is based upon the effects of the various electron fields upon each other and which employs molecular orbital rather than atomic orbital. Each such orbital characterizing the molecule as a whole is described by a definite combination of quantum numbers and possesses relative energy value.

a) *For diatomic species having (1-20)e⁻s*

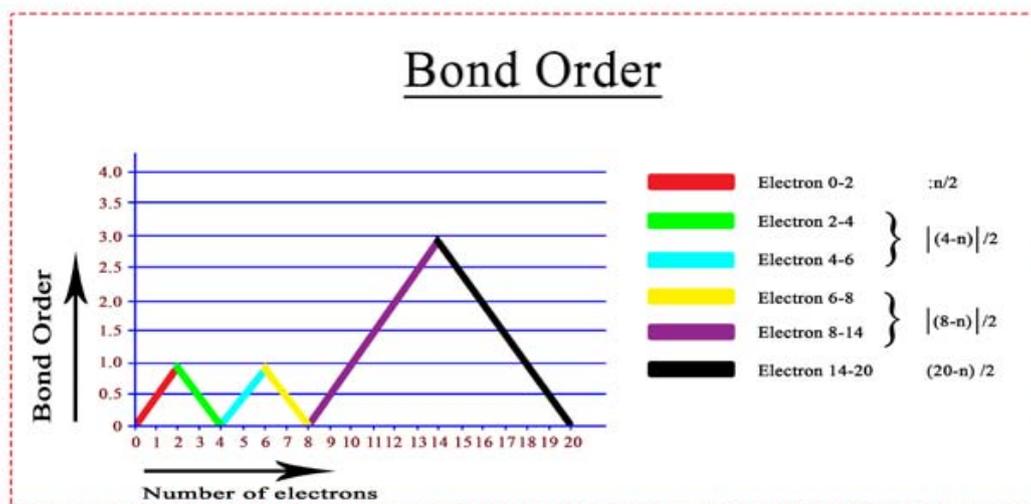*Graphical Representation of B.O. with number of electrons*

Fig. 2: (B.O. vs number of electrons)

The graphical representation presented in Fig.2 shows that bond-order gradually increases to 1 in the range (0-2) electrons then falls to zero in the range (2-4) electrons then it further rises to 1 for (4-6) electrons and once again falls to zero for (6-8) electrons then again rises to 3 in the range (8-14) electrons and then finally falls to zero for (14-20) electrons. For total no of electrons 2, 6 and 14, one can use multiple formulae, because they fall in the overlapping region in which they intersect with each other.

First of all I classify the molecules or ions into the following four (4) types based on total number of electrons present in them.

i) *Molecules and ions having total no of electrons within the range (1-2)*
In such case *Bond order = n/2;* [Where n = Total no of electrons]
Eg: H_2 (Total e⁻s = 2), Therefore B.O. = n/2 = 2/2 = 1

ii) *Molecules and ions having total no of electrons within the range (2-6)*
In such case *Bond order = I 4- n I / 2;*
[Where n = Total no of electrons, 'I I' indicates Mod function i.e. the value of bond order is always positive]
Eg: Li_2^+ (5e⁻s) Therefore B.O. = I 4-5 I / 2 = 1/2 = 0.5.

iii) *Molecules and ions having total no of electrons within the range (6-14)*
In such case *Bond order = I 8-n I / 2*
Eg: CO (Total e⁻s = 6+8=14), Therefore B.O.= I 8-14 I / 2 = 3

iv) *Molecules and ions having total no of electrons within the range (14-20)*
In such case *Bond order = (20-n) / 2;* [Where n = Total no of electrons]
Eg: NO (Total e⁻s = 15), Therefore B.O. = 20-15/2 = 2.5

If bond order is zero, the molecule is unstable (does not exist), whereas, a positive value of bond order reveals that the molecule exists and is stable (Table-3).

b) *Problems on bond order of diatomic species*
Q.1. The bond order of N_2, O_2, N_2^-, O_2^- varies as
    a. $N_2 > N_2^- > O_2 > O_2^-$ b. $O_2 > N_2 > O_2^- > N_2^-$ c. $N_2 > O_2 > N_2^- > O_2^-$ d. $N_2^- > N_2 > O_2^- > O_2$
Ans: a. $N_2 > N_2^- > O_2 > O_2^-$
  B.O. – 3.0 2.5 2.0 1.5

Q.2. Among the following species, the order of first ionization energy (IE_1) is
    a. $O_2 < O_2^+ < O_2^-$ b. $O_2^+ < O_2^- < O_2$ c. $O_2^- < O_2 < O_2^+$ d. $O_2 < O_2^- < O_2^+$
Ans: c. $O_2^- < O_2 < O_2^+$ - IE_1 (Bond order α IE_1 ; Bond order trend is 1.5<2.0<2.5)

Q.3. Which of the following is the correct order of their stability ?

    a. $CN < NO^+ < NO^-$ b. $NO^- < CN < NO^+$ c. $NO^+ < CN < NO^-$ d. $CN < NO^- < NO^+$

Ans: b. $NO^- < CN < NO^+$ - stability (Bond order α stability ; Bond order trend is 2.0<2.5<3.0)

Q.4. In which case bond order increases ?

    a. O_2 changes to O_2^+ b. N_2 changes to N_2^+ c. NO changes to NO^- d. In all cases

Ans: a. O_2 changes to O_2^+ (bond order increases from 2.0 to 2.5)

Q.5. Which of the following is the correct order of their stability ?

    a. $N_2 > N_2^+ > N_2^-$ b. $N_2 > N_2^- > N_2^+$ c. $N_2^+ > N_2 > N_2^-$ d. None of these

Ans: a. $N_2 > N_2^+ > N_2^-$ (Bond order of N_2 = 3.0, N_2^+ & N_2^- = 2.5; Bond order α stability; but when bond order be same then cationic species will have higher stability than anionic species due to increase in electron in higher energetic ABMO in anionic species)

Table 3: [Bond order values of diatomic species having (1-20)e⁻s]

Species (Molecules or ions)	Total Number of e⁻s (n)	Bond-Order (B.O.)
Bond-Order Values for the species having (1-2)e⁻s ; Bond order = n/2		
H_2^+	1	0.5
H_2, He_2^{2+}	2	1
Bond-Order Values for the species having (2-6)e⁻s ; Bond order = | 4- n | / 2		
H_2^-, He_2^+	3	0.5
He_2,	4	0
Li_2^+, He_2^-	5	0.5
Li_2, He_2^{2-}, Be_2^{2+}	6	1
Bond-Order Values for the species having (6-14)e⁻s ; Bond order = | 8- n | / 2		
Be_2^+, Li_2^-	7	0.5
Be_2, Li_2^{2-}	8	0
Be_2^-, B_2^+	9	0.5
B_2, Be_2^{2-}, HF	10	1
B_2^-, C_2^+	11	1.5
C_2, B_2^{2-}, N_2^{2+}, CN^+	12	2
C_2^-, N_2^+	13	2.5
N_2, CO, NO^+, C_2^{2-}, CN^-, O_2^{2+}	14	3
Bond-Order Values for the species having (14-20)e⁻s ; Bond order = (20-n) / 2		
N_2^-, NO, O_2^+	15	2.5
NO^-, O_2	16	2
O_2^-	17	1.5
F_2, O_2^{2-}, HCl	18	1
F_2^-	19	0.5
Ne_2	20	0

IV. PREDICTING BOND-ORDER OF OXIDE BASED ACID RADICALS

In case of oxide based acid radicals

Bond Order (B.O.) = Valency of the peripheral atom + (Charge on Acid Radical / Total number of peripheral atoms)

Eg:

ClO_4^-: (Valency of one Peripheral atom Oxygen = 2, Charge on acid radical = -1, Total Number of Peripheral atoms = 04), Therefore B.O. = 2 + (-1/4) = 1.75

ClO_3^-: (Valency of one Peripheral atom Oxygen = 2, Charge on acid radical = -1, Total Number of Peripheral atoms = 03), Therefore B.O. = 2 + (-1/3) = 1.66

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ClO$_2$$^-$: (Valency of one Peripheral atom Oxygen = 2, Charge on acid radical = -1, Total Number of Peripheral atoms = 02), Therefore B.O. = 2 + (-1/2) = 1.5

AsO$_4$$^{3-}$: (Valency of one Peripheral atom Oxygen = 2, Charge on acid radical = -3, Total Number of Peripheral atoms = 04), Therefore B.O. = 2 + (-3/4) = 1.25

AsO$_3$$^{3-}$: (Valency of one Peripheral atom Oxygen = 2, Charge on acid radical = -3, Total Number of Peripheral atoms = 03), Therefore B.O. = 2 + (-3/3) = 1.0

SO$_4$$^{2-}$: (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = -2, Number of Peripheral atoms = 04), Therefore B.O. = 2 + (-2/4) = 1.5

SO$_3$$^{2-}$: (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = -2, Number of Peripheral atoms = 03), Therefore B.O. = 2 + (-2/3) = 1.33

PO$_4$$^{3-}$; (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = -3, Number of Peripheral atoms = 04), Therefore B.O. = 2 + (-3/4) = 1.25

BO$_3$$^{3-}$; (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = -3, Number of Peripheral atoms = 03), Therefore B.O. = 2 + (-3/3) = 1

CO$_3$$^{2-}$; (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = -2, Number of Peripheral atoms = 03), Therefore B.O. = 2 + (-2/3) = 1.33

SiO$_4$$^{4-}$: (Valency of Peripheral atom Oxygen = 2, Charge on acid radical = - 4, Number of Peripheral atoms = 04), Therefore B.O. = 2 + (- 4/4) = 1

Bond order is a measure of the strength of the bond between two atoms. Bond order can be applicable to make a comparison of some characteristics between (among) the molecules as

B.O. α 1 / Bond length (BL) or Bond distance (BD);
B.O. α Bond strength (BS);
B.O. α Bond dissociation Energy (BDE);
B.O. α Bond Energy (BE);
B.O. α Ionization Energy (IE);
B.O. α Thermal Stability;
B.O. α 1 / Reactivity (R)

Correlation among / between Literature values of bond-distances of some oxide based acid radicals with their predicted bond order values:

Literature values of the Cl-O average bond lengths in ClO_4^-, ClO_3^- and ClO_2^- ; As-O bond lengths in AsO_4^{3-} and AsO_3^{3-} with respect to their bond order values suggest that with increasing bond-order M-O bond length (Where M = Cl, As etc.) decreases which is shown in Table-4.

Table 4: (Correlation of some bond-distances with their predicted bond order values)

Oxide Based Acid Radicals	Bond-Order Values	Avg. M-O Bond-Distances As per Literature (Å)	Remarks
ClO_4^-	1.75	1.50	Increasing Bond-Order decreases Bond Length
ClO_3^-	1.6	1.57	
ClO_2^-	1.5	1.64	
AsO_4^{3-}	1.25	1.75	
AsO_3^{3-}	1.0	1.77	

Correlation among / between Literature values of bond dissociation energy (KJ mol^{-1}) of some molecules or ions with their predicted bond order values (Table-5):

Table 5: (Correlation of some bond dissociation energy with their predicted bond order values)

Molecules or ions	Bond-Order Values	Dissociation energy (KJ mol^{-1})	Remarks
O_2^+	2.5	642.9	Increasing Bond-Order increases Bond dissociation energy (BDE)
O_2	2.0	493.6	
O_2^-	1.5	395.0	
NO^+	3.0	1046.9	
NO	2.5	826.9	
NO^-	2.0	487.8	

Table 6: (Magnetic moments of diatomic species)

Species (Molecules or ions)	Total Number of e⁻s	Number of unpaired electrons (n)	Magnetic moment (μ_s) in Bohr Magneton (B.M.)	Remark on magnetic behavior
H_2^+	1	1	1.73	Para magnetic
H_2, He_2^{2+}	2	0	0	Diamagnetic
H_2^-, He_2^+	3	1	1.73	Para magnetic
He_2,	4	0	0	Diamagnetic
Li_2^+, He_2^-	5	1	1.73	Para magnetic
Li_2, He_2^{2-}, Be_2^{2+}	6	0	0	Diamagnetic
Be_2^+, Li_2^-	7	1	1.73	Para magnetic
Be_2, Li_2^{2-}	8	0	0	Diamagnetic
Be_2^-, B_2^+	9	1	1.73	Para magnetic
B_2, Be_2^{2-}, HF	10	2	2.82	Para magnetic
B_2^-, C_2^+	11	1	1.73	Para magnetic
C_2, B_2^{2-}, N_2^{2+}, CN^+	12	0	0	Diamagnetic
C_2^-, N_2^+	13	1	1.73	Para magnetic
N_2, CO, NO^+, C_2^{2-}, CN^-, O_2^{2+}	14	0	0	Diamagnetic
N_2^-, NO, O_2^+	15	1	1.73	Para magnetic
NO^-, O_2	16	2	2.82	Para magnetic
O_2^-	17	1	1.73	Para magnetic
F_2, O_2^{2-}, HCl	18	0	0	Diamagnetic
F_2^-	19	1	1.73	Para magnetic
Ne_2	20	0	0	Diamagnetic

Problems on Magnetic behavior of diatomic species:

Q.1. Which of the following species is diamagnetic ?

　　a. B_2　　　b. N_2^+　　　c. N_2^-　　　d. N_2^{2+}

Ans: d. N_2^{2+} (Total electrons 12, n = 0, Magnetic moment, μ_s = 0 B.M.)

Q.2. Number of unpaired electrons in CO molecule is

　　a. 0　　　b.1　　　c. 2　　　d. 3

Ans: a. 0 (Table - 6)

VI. EVALUATING SPIN MULTIPLICITY

　　　Spin-multiplicity value and its corresponding spin state was first discovered by Friedrich Hund in 1925. The formula which is generally used for the prediction of spin multiplicity value is [(2S+1), where S = Σs = total spin quantum no] is time consuming. To keep the matter in mind a simple innovative method has to be introduced for calculation of spin-multiplicity value and thus its corresponding spin state, shown in Table-7, in the easiest way by ignoring the calculation of total spin quantum number (S = Σs).

　　　First of all we should classify the species (atoms, molecules, ions or complexes) for which spin multiplicity value should be evaluated into three types based on the nature of alignment of unpaired electrons present in them.

a) Species having unpaired electrons in upward alignment (↑)

In this case, spin multiplicity = (n+1); where n = number of unpaired electrons

　　　Spin multiplicity = (n +1) = (1+1) = 2 (spin state = doublet); (2+1) = 3 (spin state = triplet) and (3 + 1) = 4 (spin state = quartet) respectively.

Spin multiplicity = (n +1) = (2 + 1) = 3 (in this case ignore paired electrons) (spin state = triplet) and (1+1) = 2 (spin state = doublet)

↑↓	↑↓	↑↓

Spin multiplicity = (n +1) = (0 + 1) = 1 (spin state = singlet)

b) *Species having unpaired electrons in downward alignment (↓)*

In this case spin multiplicity = (-n+1)

Here (-ve) sign indicate downward arrow.

↓		

↓	↓	

↓	↓	↓

Spin multiplicity = (-n +1) = (-1 + 1) = 0; (-2 + 1) = -1 and (-3 + 1) = -2 respectively.

↑↓	↓	↓

↑↓	↑↓	↓

Spin multiplicity = (-n + 1) = (-2 + 1) = -1(ignore paired electrons) and (-1 + 1) = 0 respectively.

c) *Species having unpaired electrons in both mixed alignment (↑)(↓)*

In this case spin multiplicity = [(+n) + (-n) + 1]

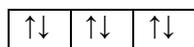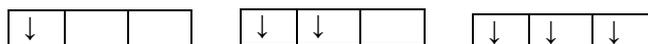where, n = number of unpaired electrons in each alignment. Here, (+ve) sign and (–ve) sign indicate upward and downward alignment respectively.

↑	↓	

Here total no of unpaired electrons = 2 in which one having upward direction (+1) and other having downward mode (-1).
Hence Spin multiplicity = [(+n) + (-n) +1] = [(+1) + (-1) + 1] = 1 (spin state = singlet)

↑	↑	↓

Here the total no of unpaired electrons = 3 in which two unpaired electrons lie in upward (+2) and one unpaired electrons lie in downward (-1) .
Hence Spin multiplicity = [(+n) + (-n) + 1] = [(+2) + (-1) + 1] = 2 (spin state = doublet)

↑	↓	↑	↓	↑

Here the total no of unpaired electrons = 5 in which three unpaired electrons lie upward (+3) and two unpaired electrons lie downward (-2).
Hence Spin multiplicity = [(+n) + (-n) + 1] = [(+3) + (-2) +1] = 2 (spin state = doublet)

Table 7: (Spin multiplicity and corresponding Spin State)

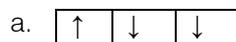| Number of unpaired electrons (n)	Spin multiplicity value (n + 1)	Spin state
0	1	Singlet
1	2	Doublet
2	3	Triplet
3	4	Quartet
4	5	Quintet
5	6	Multiplet

Problems on spin multiplicity and spin state:

Q.1. Which one of the following will have spin multiplicity value 1 ?

    a. B_2 b. B_2^+ c. B_2^- d. B_2^{2-}

Ans: d.B_2^{2-} (Total electrons 12, number of unpaired electrons=0,spin multiplicity= n + 1 = 0 + 1= 0)

Q.2. Which one of the following electronic representation will have zero spin multiplicity value

a. | ↑ | ↓ | ↓ |

b. | ↑ | ↓ | ↑ | ↓ | ↑ |

Ans: a. | ↑ | ↓ | ↓ | Spin multiplicity = [(+n) + (-n) + 1] = [+1 – 2 + 1] = 0

Q.3. Which one of the following molecules or ions will have triplet spin state ?
    a. NO   b. CO   c. NO^+ d. NO^-
Ans: d. NO^- (Total electrons = 16, Unpaired electrons, n = 02
                    spin multiplicity = +n + 1 = +2 + 1 = 3, spin state = triplet)

VII. Calculating of Chemical Bonds (π-Bonds, σ-Bonds, Single and Double Bonds) in Open Chain and Cycloalkene Systems

The molecular formula which defines a very large number of chemical structure, in this particular case, it is a herculean task to calculate the nature and number of bonds. Earlier Badertscher *et al* studied a novel formalism to characterize the degree of unsaturation of organic molecules. But no such work has not been taken till now to calculate the number and types of bonds in open chain olefinic system having complex molecular formulae like $C_{176}H_{250}$, $C_{2000}H_{2000}$.

Keeping this in view, a rapid innovative method has been proposed for the calculation of number of π-bonds, σ-bonds, single and double bonds with the help of following 06 (six) completely new formulae for certain aliphatic unsaturated open chain and cyclic olefinic hydrocarbons.

a) For Open Chain Aliphatic Hydrocarbons
 i. *Calculation of π-bonds and double bonds (P)*
The number of π bonds or double bonds for a straight chain olefin is

$$P = [(2X-Y)/2] + 1$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and P = number of π bonds/double bonds. *E.g.:* In $C_{176}H_{250}$, X = 176, Y = 250, therefore P = (2 x 176 – 250)/2 +1 = 51 + 1 = 52 number of π bonds or double bonds.

 ii. *Calculation of σ-bonds (S)*
The number of σ bonds for a straight chain olefin is

$$S = [X + Y - 1]$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and S = number of sigma bonds (σ-bonds).

E.g.: In $C_{176}H_{250}$, X = 176, Y = 250, therefore P = 176 + 250 -1 = 425 σ bonds.

 iii. *Calculation of Single bonds (A)*
The total number of single bond for a straight chain olefin is

$$A = [(3Y/2)-2]$$

where A = number of single bonds and Y is number of hydrogen atoms.

E.g.: In $C_{176}H_{250}$, Y = 250, therefore A = [(3 x 250)/2] = 375 -2 = 373 single bonds. Examples have been illustrated in Table-8.

b) For Cyclic aliphatic olefinic hydrocarbons
 i. *Calculation of π-bonds and double bonds (P_c)*
The number of π bonds or double bonds for an aliphatic cyclic olefin is

$$P_c = [(2X-Y)/2]$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and P_c = number of π bonds or double bonds in the cyclic olefinic system.

E.g.: In cyclooctatetraene (C_8H_8), X = Y = 8, therefore P_c = 16-8/2 = 4 number of π bonds or double bonds.

ii. *Calculation of σ-bonds (S_c)*

The number of σ bonds for an aliphatic cyclic olefin is S_c = [X + Y]

Where, X = number of carbon atoms; Y = number of hydrogen atoms and S_c = number of sigma bonds (σ- bonds) in cyclic olefinic system.

Eg: In cyclooctatetraene (C_8H_8), X = Y = 8, therefore S_c = 8+8 = 16 number of σ bonds.

iii. *Calculation of Single bonds (A_c)*

The total number of single bonds in aliphatic cyclic olefin can be calculated by using the formula A_c = [3Y/2]

Where, A_c = number of single bonds and y is number of hydrogen atoms in aliphatic cyclic olefin.

E.g.: In cyclooctatetraene (C_8H_8), Y = 8, therefore A_c = 24/2 = 12 number of single bonds. Examples have been illustrated in Table-9.

Table 8: Calculation of bonds in open chain olefinic hydrocarbons

Example (C_xH_y)	Straight-chain Structure	π bond/ bonds [(2X-Y)/2+1]	σ bonds [X+Y-1]	Single bonds [(3Y/2)-2]	Double bond/bonds [(2X-Y)/2 + 1]
C_2H_4	$H_2C=CH_2$	1	5	4	1
C_3H_6	$H_2C=CH-CH_3$	1	8	7	1
C_3H_4	$H_2C=C=CH_2$	2	6	4	2
C_4H_8	i)$H_2C=CH-CH_2-CH_3$ ii)$H_3C-HC=CH-CH_3$	1	11	10	1
C_4H_6	i)$H_2C=C=CH-CH_3$ ii)$H_2C=CH-CH=CH_2$	2	9	7	2
C_4H_4	$H_2C=C=C=CH_2$	3	7	4	3
$C_{176}H_{250}$	-	52	425	373	52
$C_{2000}H_{2000}$	-	1001	3999	2998	1001
$C_{99}H_4$	-	98	102	4	98

Table 9: Calculation of Bonds in Cyclo Alkene System

Example (C_xH_y)	Cycloalkene	π bond / bonds (P_c) = [(2X-Y)/2]	σ bonds (S_c) [X+Y]	Single bonds (A_c) [(3Y/2)]	Double bond/bonds [(2X-Y)/2]
C_3H_4	Cyclopropene	1	7	6	1
C_4H_4	Cyclobutadiene	2	8	6	2
C_5H_6	Cyclopentadiene	2	11	9	2
C_6H_8	Cyclohexadiene	2	14	12	2
C_7H_8	Cycloheptatriene	3	15	12	3
C_8H_8	Cyclooctatetraene	4	16	12	4

VIII. Calculation of π-Bonds, σ-Bonds, Single and Triple Bonds in Straight Chain Alkyne And Cycloalkyne Systems

The number and types of bonds in open chain and cycloalkynes having complex molecular formula is a Herculean task. Keeping this in view, a rapid innovative method has been proposed for the calculation of number of π-bonds, σ-bonds, single and triple bonds with the help of following 08 (eight) completely new formulae by just manipulating the number of carbon and hydrogen atoms by using some factors for certain aliphatic unsaturated open chain and cycloalkynes.

a) *Open Chain Aliphatic Alkynes*

i. *Calculation of π-bonds (P)*

The number of π bonds for an aliphatic open chain alkyne, where there is one or more than one triple bonds is P= [{(2X-Y)/2} + 1]

Where, X = number of carbon atoms; Y = number of hydrogen atoms and P = number of π bonds.

E.g.: In $C_{16}H_{30}$, X = 16, Y = 30, therefore P = [{(2X-Y)/2} + 1] = [{(2 x 16 – 30)/2} +1] = 2 number of π bonds.

ii. *Calculation of σ-bonds (S)*

The number of σ bonds for an aliphatic open chain alkyne, where there is one or more than one triple bonds is S= [X+Y-1]

Where, X = number of carbon atoms; Y = number of hydrogen atoms and S = number of σ bonds.

E.g.: In $C_{16}H_{30}$, X = 16, Y = 30, therefore, S= [X+Y-1] = [16+30-1] = 45 numbers of σ bonds.

iii. *Calculation of Single bonds (A)*

The total number of single bond for an aliphatic open chain alkyne, where there is one or more than one triple bonds is A = [{(2X+5Y)/2} - 3]/2

Where, A = number of single bonds, X = number of carbon atoms and Y = number of hydrogen atoms.

E.g.: In $C_{16}H_{30}$, X = 16, Y = 30, therefore, A = [{(2X+5Y) / 2} - 3]/2

$$= [\{(2x16+5x30)/2\}-3]/2 = [91-3]/2$$

$$= 44 \text{ numbers of single bonds.}$$

iv. *Calculation of Triple bonds (T)*

In the first case, we have to count the number of carbon atoms (X) and the number of hydrogen atoms (Y) in a given unsaturated hydrocarbon containing triple bonds. The formula to calculate the number of triple bonds for an aliphatic open chain alkyne, where there is one or more than one triple bonds is

$$T= [\{(2X-Y)/2\} + 1]/2$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and T = number of triple bonds.

E.g.: In $C_{16}H_{30}$, X = 16, Y = 30, therefore, T = [{(2X-Y)/2} + 1]/2

$$= [\{(2 \text{ x } 16 – 30)/2\} +1]/2$$

$$= 2/2 = 1 \text{ triple bond.}$$

Examples have been illustrated in Table-10.

b) *Cycloalkynes*

i. *Calculation of π-bonds (P_c)*

In the first case, we have to count the number of carbon atoms (X) and the number of hydrogen atoms (Y) in the given unsaturated cycloalkyne.

The number of π bonds for an aliphatic cycloalkyne is

$$P_c= [(2X-Y)/2]$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and P_c = number of π bonds in the cycloalkyne system.

E.g.: In Cycloheptyne (C_7H_{10}), X =7, Y = 10, therefore P_c = (2x7-10)/2 = 2 number of π bonds.

ii. *Calculation of σ-bonds (S_c)*

The number of σ bonds for an aliphatic cycloalkyne is

$$S_c = [X + Y]$$

Where, X = number of carbon atoms; Y = number of hydrogen atoms and S_c = number of sigma bonds (σ-bonds) in cyclo alkyne system.

E.g.: In Cycloheptyne (C_7H_{10}), X =7, Y = 10, therefore S_c = (7+10) = 17 number of σ bonds.

iii. *Calculation of Single bonds (A_c)*

The total number of single bond for an aliphatic cycloalkyne is

$$A_c = [\{(2X+5Y)/2\}]/2$$

Where, A_c = number of single bonds in cycloalkyne, X = number of carbon atoms and Y = number of hydrogen atoms.

E.g.: In Cycloheptyne (C_7H_{10}), X = 7, Y = 10, therefore, A_c = [{(2X+5Y)/2}]/2

$$= [\{(2 \times 7 + 5 \times 10)/2\}]/2 = 32/2 = 16 \text{ numbers of single bonds.}$$

iv. *Calculation of Triple bonds (T)*

The number of triple bond is T_c = [{(2X-Y)/2}]/2

Where, X = number of carbon atoms;

Y = number of hydrogen atoms and

T_c = number of triple bond.

E.g.: In Cycloheptyne (C_7H_{10}), X = 7, Y = 10, therefore, T_c = [{(2X-Y)/2}]/2 = [{(2 × 7 – 10)/2}]/2 = 2/2 = 1 triple bond.

Table 10: Calculation of bonds in open chain Alkyne system)

Example for Open Chain Alkyne (C_xH_y)	π bonds [{(2X-Y)/2} + 1]	σ bonds [X+Y-1]	Single bonds [{(2X+5Y)/2} - 3]/2	Triple bond/bonds [{(2X-Y)/2} + 1]/2
$C_{10}H_{18}$	2	27	26	1
$C_{11}H_{20}$	2	30	29	1
$C_{12}H_{22}$	2	33	32	1
$C_{13}H_{24}$	2	36	35	1
$C_{14}H_{26}$	2	39	38	1
$C_{15}H_{28}$	2	42	41	1
$C_{16}H_{30}$	2	45	44	1
C_6H_6	4	11	9	2
$C_{12}H_{14}$	6	25	22	3

IX. CONCLUSIONS

It may be expected that these innovative methods would go a long way to help to the students of chemistry at Undergraduate, Senior Undergraduate and Post-Graduate level who would choose the subject as their career. Experiment *in vitro* on 100 students showed that by using these new innovative methods students can save up to 30-40 mins time in the examination hall. On the basis of this, I can strongly recommend to use these new time economic interesting pedagogies.

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