

MOLECULAR ORBITAL THEORY ✓

VALENCE BOND THEORY ✓

CRYSTAL FIELD THEORY ✓

LIGAND AND TYPES

PERIODIC TABLE ✓

CO-ORDINATION COMPOUND.

1 Molecular Orbital Theory

2 Overlap of orbitals

3 Valence bond theory

4 Crystal field Theory

(a) Splitting of d-orbitals by electrostatic field

(b) Adjusted Crystal field theory.

(c) ESP Electron spin resonance

(d) NMR Nuclear magnetic resonance.

(e) Nephelauxetic effect. (f) Intensities of d-d transition

5. Hydrogen bonding

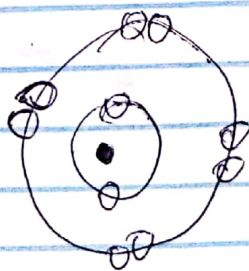
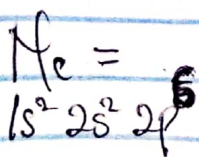
6. The periodic table

(a) Versions of the periodic table

(b) Variations of physical properties in the periodic table

7. Coordination Compound (a) Types of ligands.

Stability of close shell



First ionization energy I_1 of Ne is very high because the electrons in the p-shell shield each other from the Z_{eff} and also because the outermost shell p, is stable.

13/2019

MOLECULAR ORBITAL THEORY [Dr. Lawal]

Molecular orbital theory assumes that individual electron pairs are found in molecular orbitals that are distributed over the entire molecule.

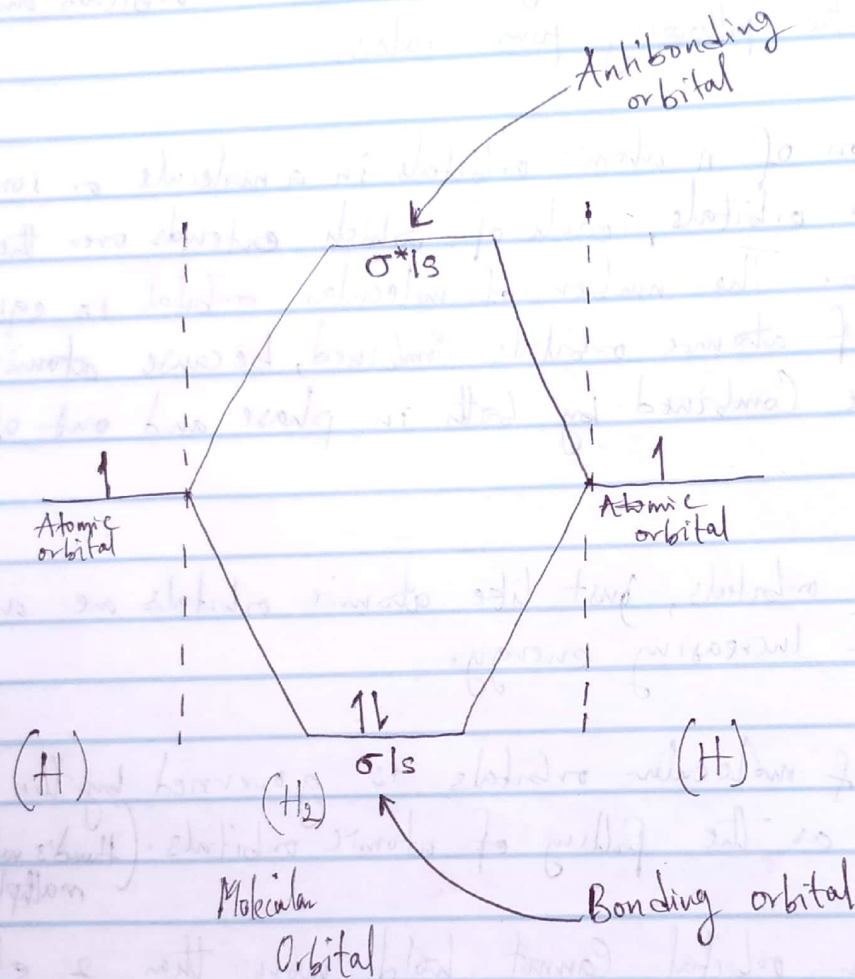
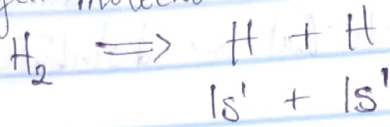
Molecular orbitals are analogous to atomic orbitals and are described by the following four rules:

- i. Combination of n atomic orbitals in a molecule or ion forms n molecular orbitals, each of which extends over the entire molecule or ion. The number of molecular orbitals is equal to the number of atomic orbitals combined, because atomic orbitals can be combined by both in phase and out of phase addition.
- ii. Molecular orbitals, just like atomic orbitals are arranged in order of increasing energy.
- iii. Filling of molecular orbitals is governed by the same principles as the filling of atomic orbitals. (Hund's rule of maximum multiplicity)
 - * A molecular orbital cannot hold more than 2 electrons and the 2 electrons have opposite spins.
 - * When two or more degenerate (same energy) molecular orbitals are available, one electron is placed in each before any one of them gets two electrons.
 - * When two atomic orbitals combine to form a molecular orbital, the wave functions are combined both in phase and out of phase to create one bonding molecular orbital and one antibonding molecular orbital respectively.

$$pH = -\log[H^+] + \log \frac{[A^-]}{[HA]}$$

Energy Diagrams

1. Hydrogen molecule



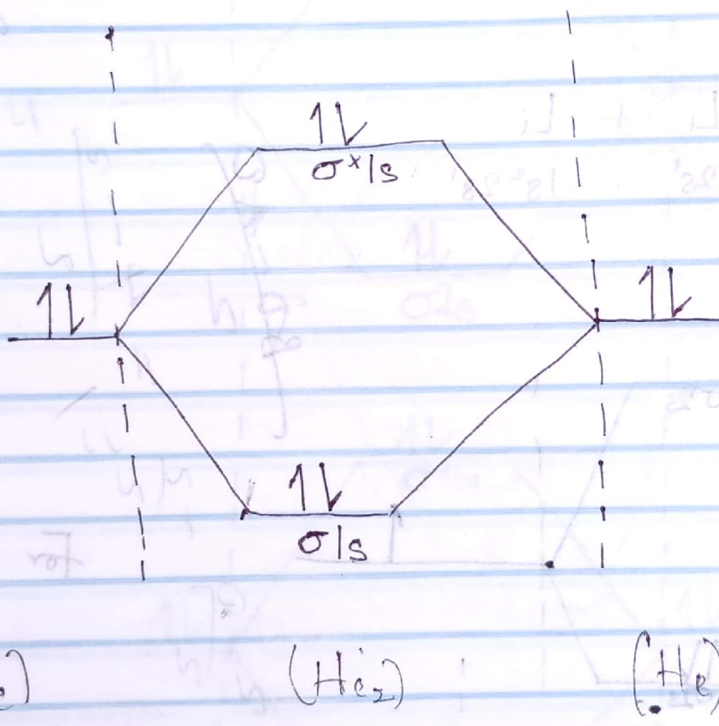
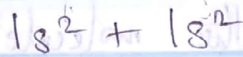
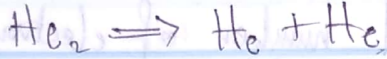
A H_2 molecule is made by superimposing (overlapping) the $1s$ orbitals of two H atoms. If the orbitals have the same phase, they will interfere constructively and form a molecular orbital with greater electron density between the positively charged nuclei. It will require less energy to hold the atoms together if there are two electrons in this orbital and the orbital is called a Bonding orbital.

If the atomic orbitals are of opposite phase, they will interfere destructively and form a molecular orbital with less electron density between the nuclei. Because the nuclei repel each other, it will take more energy to hold the atoms together in this

Configuration: This forms an Anti-bonding orbital.

Bonding orbital: Gives stability to the molecule while
 Anti-bonding orbital destabilizes the molecule.

2. Helium



Bond order

$$\text{Bond order} = \frac{\text{No. of bonding electrons} - \text{no. of antibonding electrons}}{2}$$

$$\text{OR}$$

$$\text{BO} - \text{AO}$$

$$\frac{2 - 2}{2}$$

for Hydrogen, Bond order = $(\text{BO} - \text{AO})/2 = (2 - 0)/2 = 2/2 = 1$

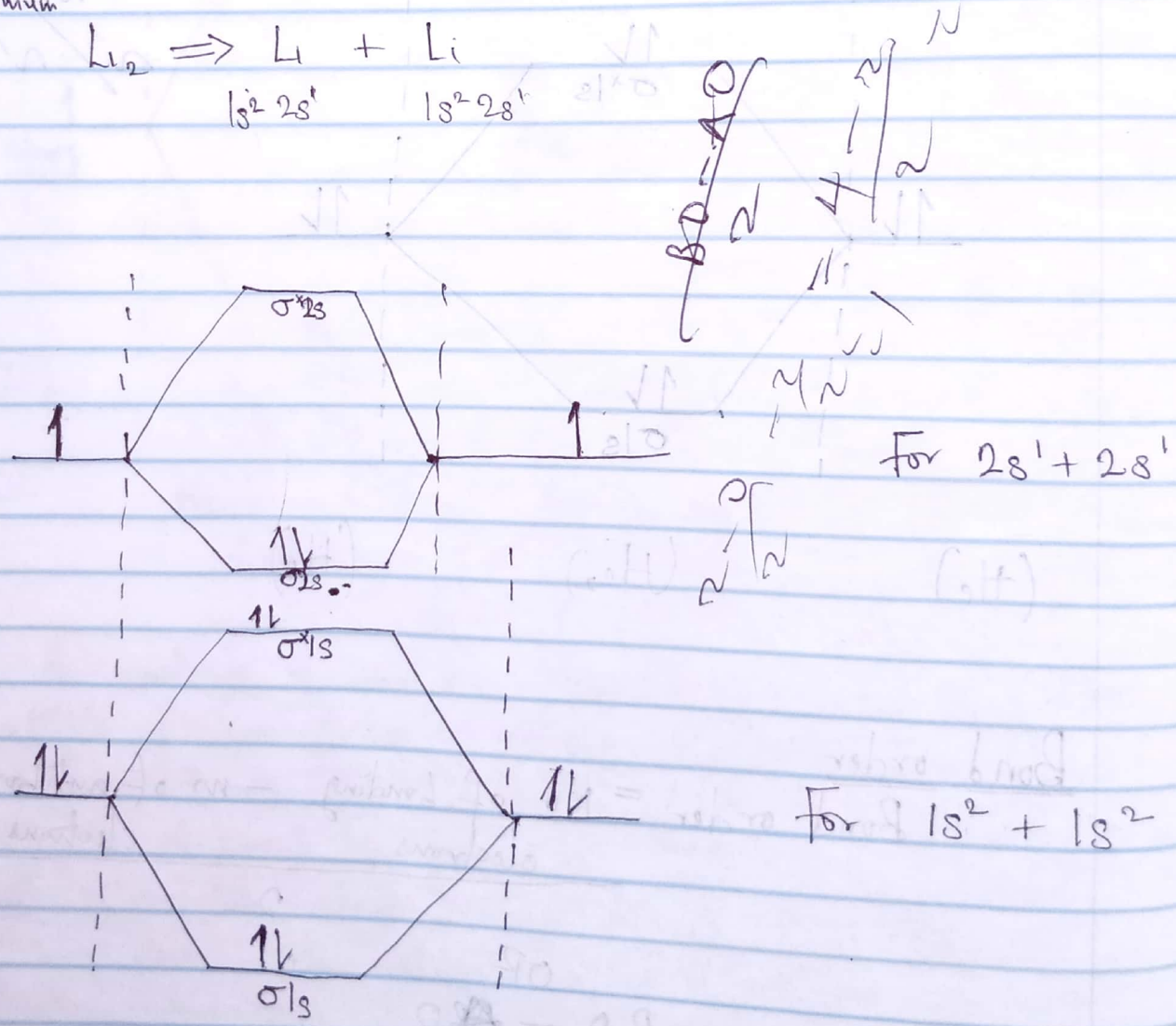
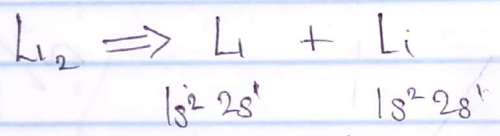
for Helium, Bond order = $(\text{BO} - \text{AO})/2 = (2 - 2)/2 = 0/2 = 0$

Note Bond order must not be $\neq 0$ for a molecule to exist therefore, since the bond order for Helium molecule is zero. The molecule does not exist.

Note The higher the bond order, the higher the stability. Bond energy is only used with Molecular orbital (MO) theory.

Note For a molecule with equal number of electrons in bonding and anti-bonding orbitals, the molecule won't exist

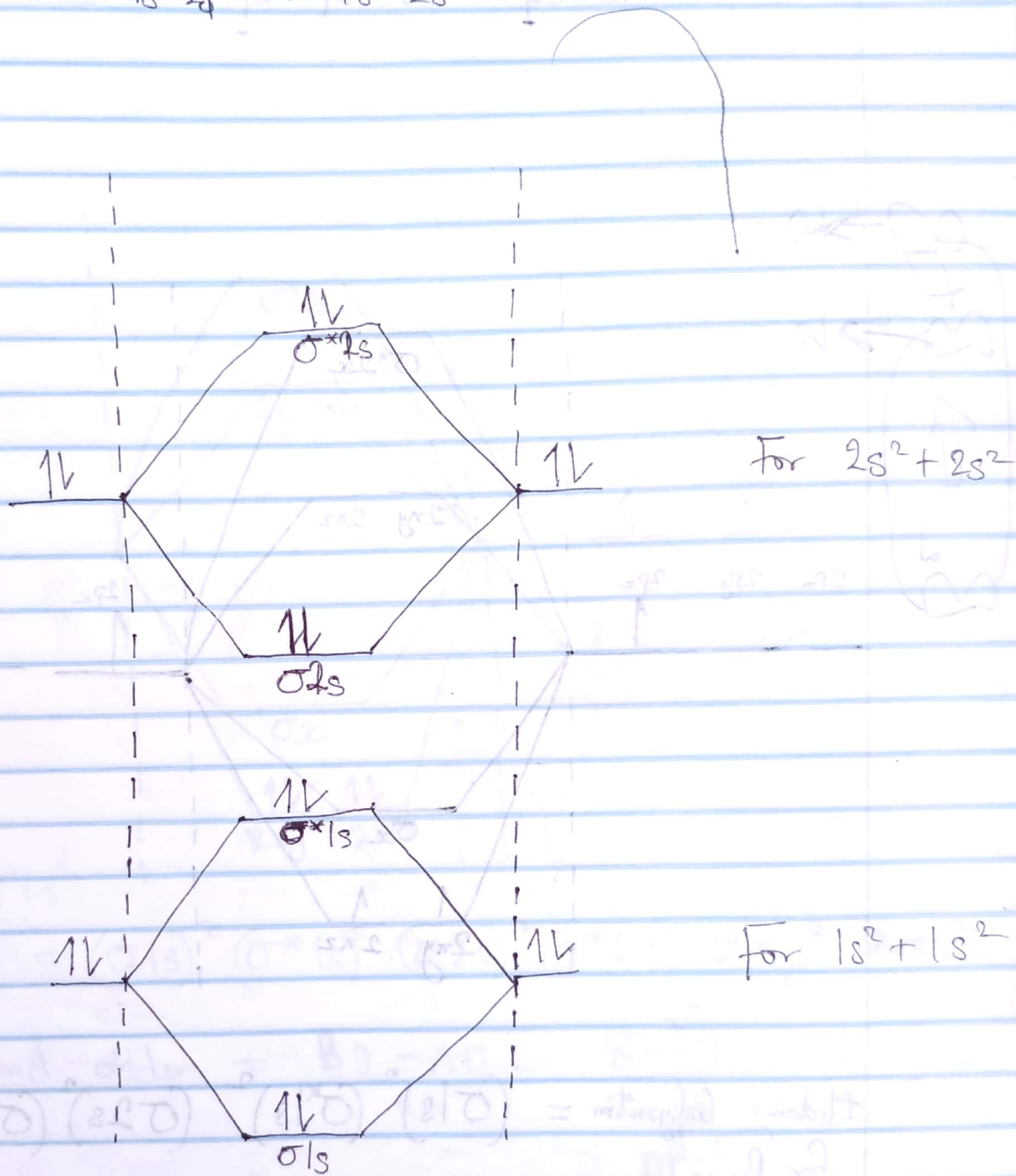
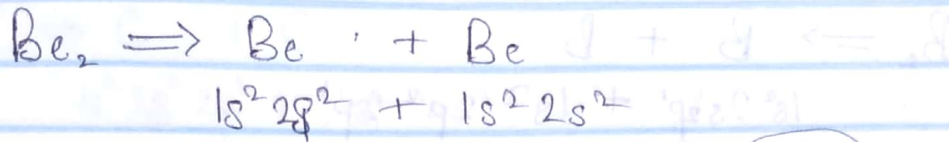
3^r Lithium



$$\text{Bond Order} = \frac{BO - AO}{2} = \frac{4 - 2}{2} = \frac{2}{2} = 1$$

Thus, Li_2 (Lithium) molecule exist (ie it's stable)

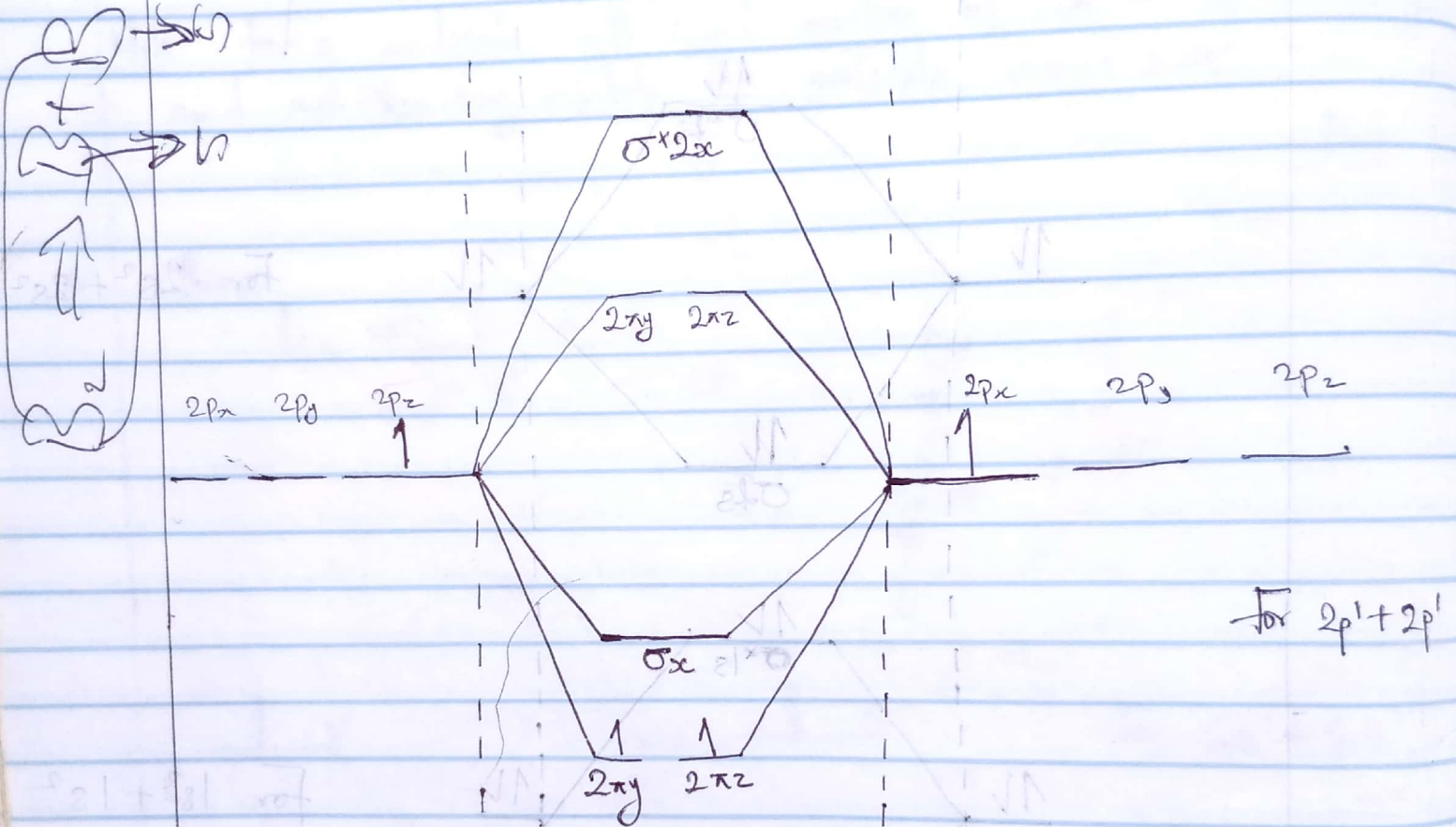
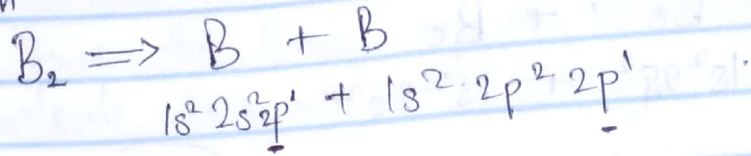
4. Beryllium



$$\text{Bond Order} = \frac{\text{BO} - \text{AO}}{2} = \frac{4 - 4}{2} = \frac{0}{2} = 0$$

Thus, Be_2 does not exist.

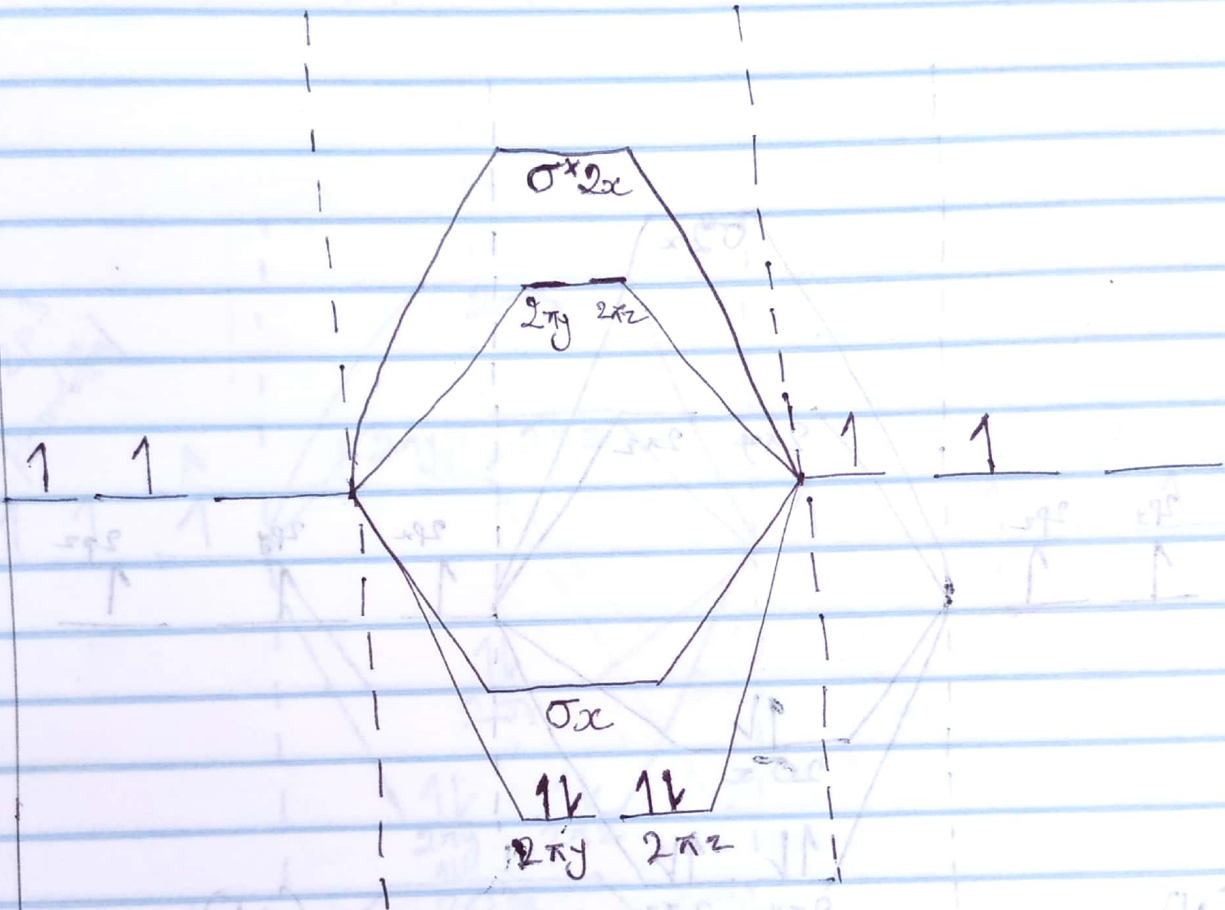
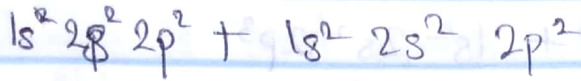
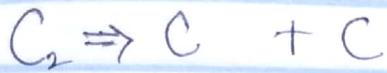
5. Boron



Electronic Configuration = $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2x)^2 (\pi 2y)^1 (\pi 2z)^1$
 for B₂

$$\text{Bond Order} = \frac{BO - AO}{2} = \frac{6 - 4}{2} = \frac{2}{2} = 1$$

6. Carbon

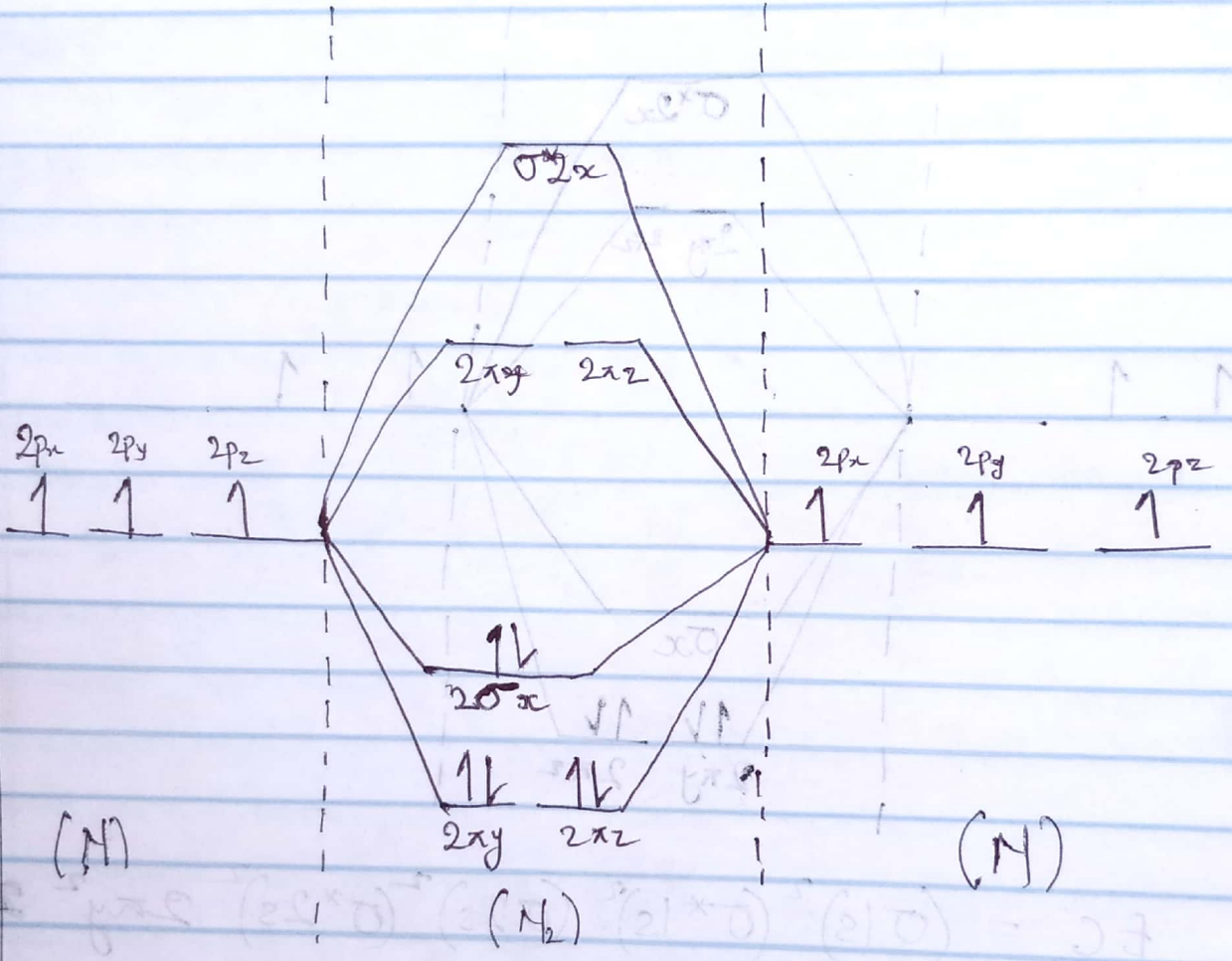
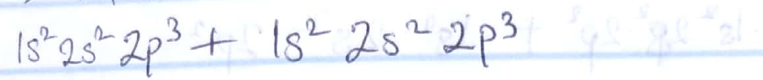
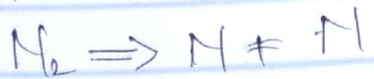


$$EC = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 2\pi_y^2 2\pi_z^2$$

$$\text{Bond order} = \frac{BO - AO}{2} = \frac{8 - 4}{2} = \frac{4}{2} = 2$$

$$\frac{4 - 0}{2} = \frac{4}{2} = 2$$

7. Nitrogen



(N)

(N)

(N₂)

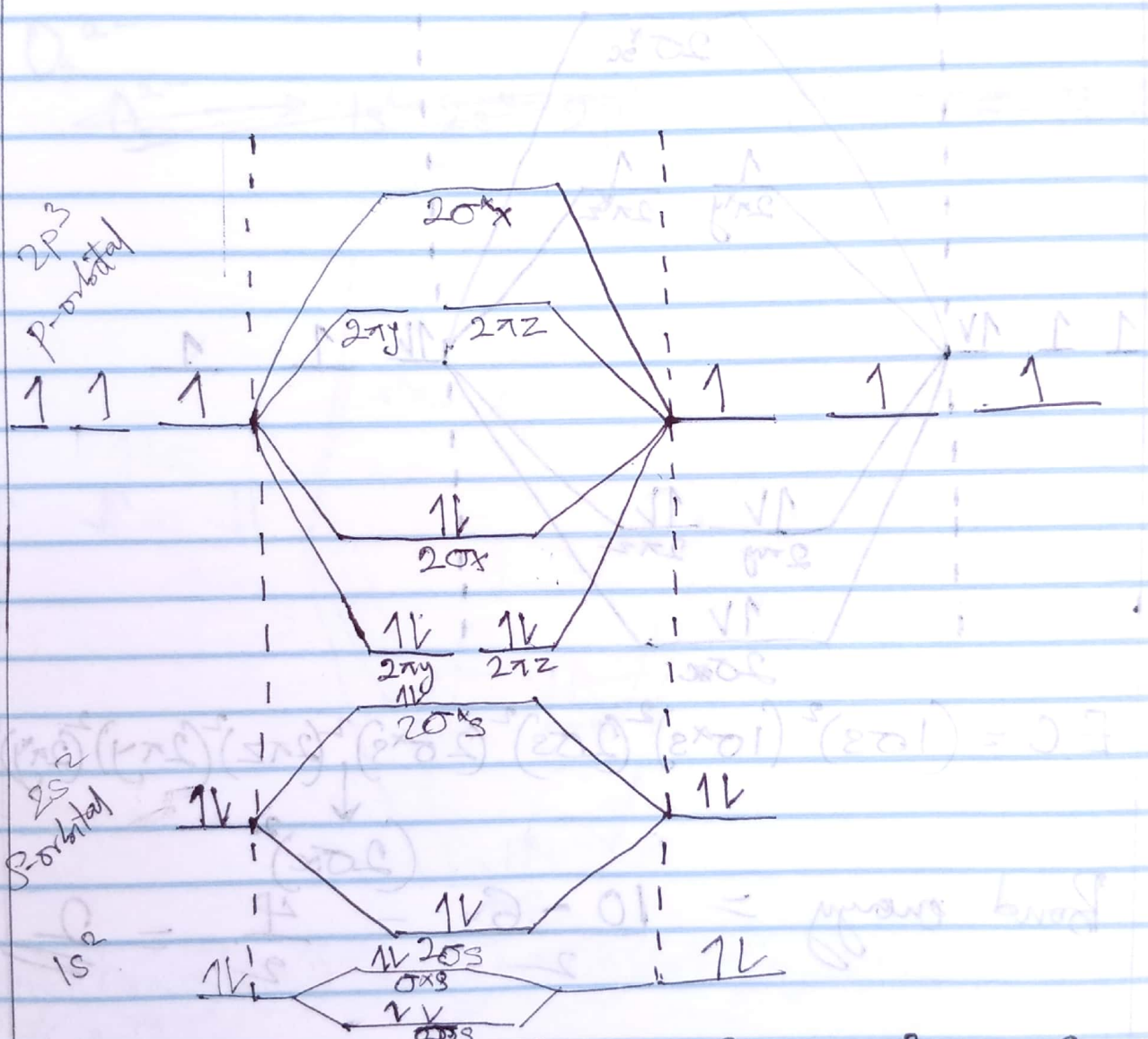
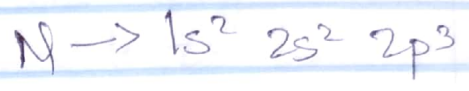
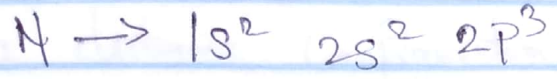
Bond Order = $\frac{BO - AO}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$

EC = $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 2\pi_y^2 2\pi_z^2 (\sigma_x)^2$

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MOLECULAR ORBITAL CONT'

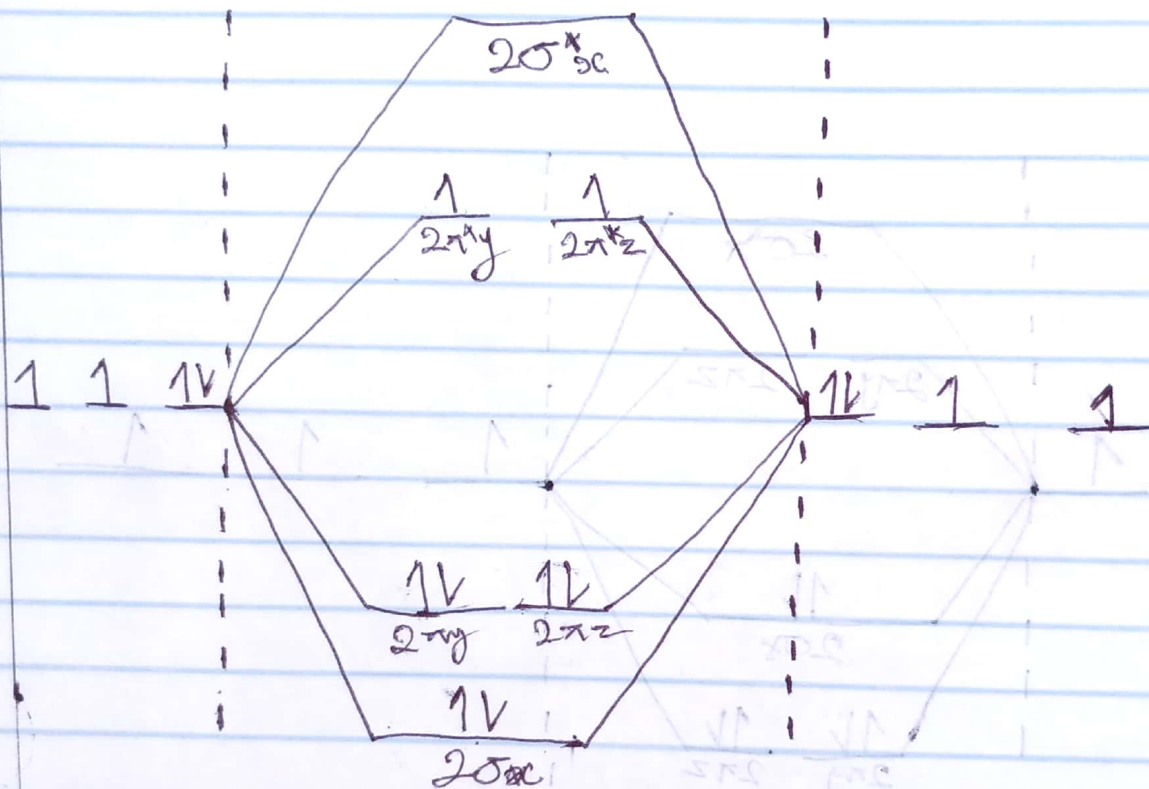
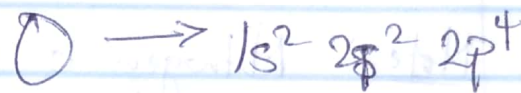
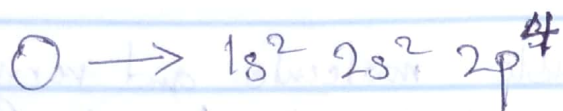
Note: Nitrogen is most stable molecule and very excess in nature but not reactive, and has the highest bond order.



$$EC = (1\sigma)^2 (1\sigma^*)^2 (2\sigma)^2 (2\sigma^*)^2 (2\pi)^2 (2\pi)^2$$

$$\text{Bond order} = \frac{BO - AO}{2} = \frac{10 - 4}{2} = \frac{6}{2} = 3$$

8. Oxygen O_2



$$EC = (1\sigma_s)^2 (1\sigma_s^*)^2 (2\sigma_s)^2 (2\sigma_s^*)^2 (2\pi_z)^2 (2\pi_y)^2 (2\pi_x)^2 (2\pi_z^*)^2$$

$$\text{Bond energy} = \frac{10 - 6}{2} = \frac{4}{2} = \underline{\underline{2}}$$

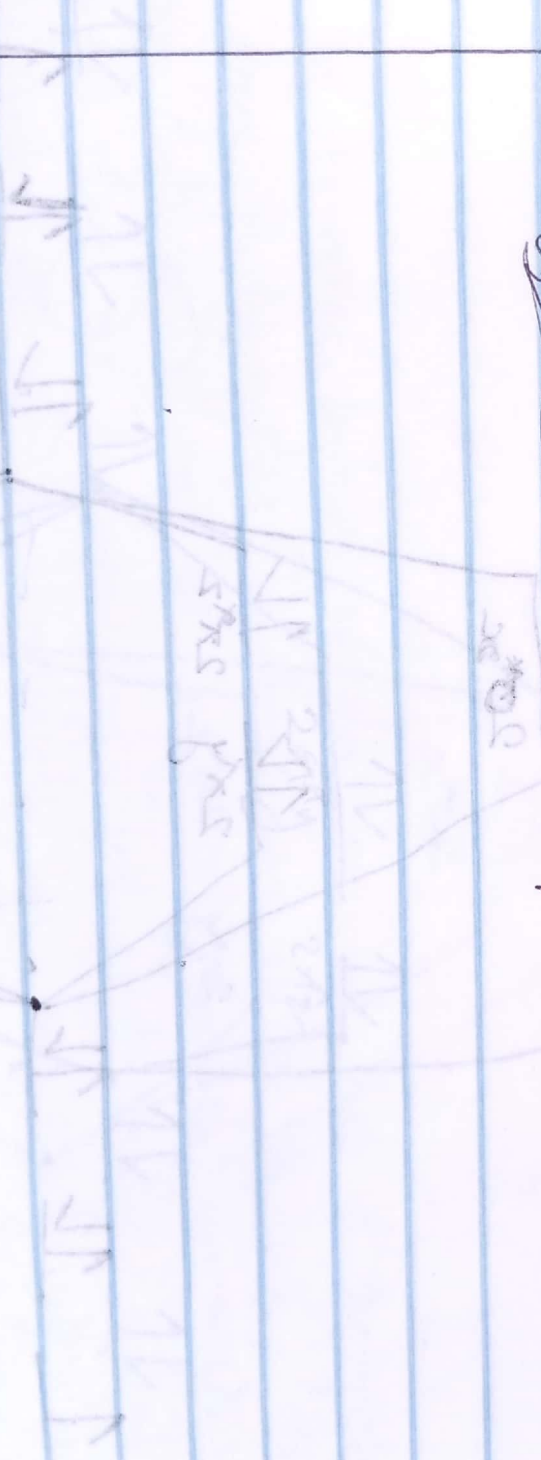
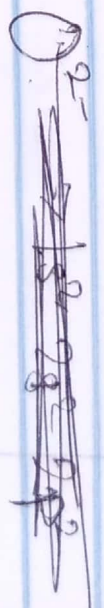
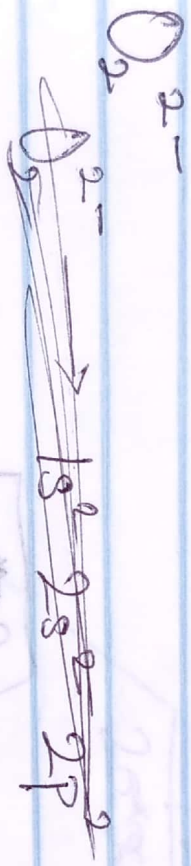
Assignment

For the following hypothetical molecule:
 O_2^{2-} , O_2^+ , O_2^{2+} , O_2 .

$O_2^{2-} \rightarrow$

1) Draw the molecular orbital energy level diagram, write the electronic configuration and calculate the bond order.

A

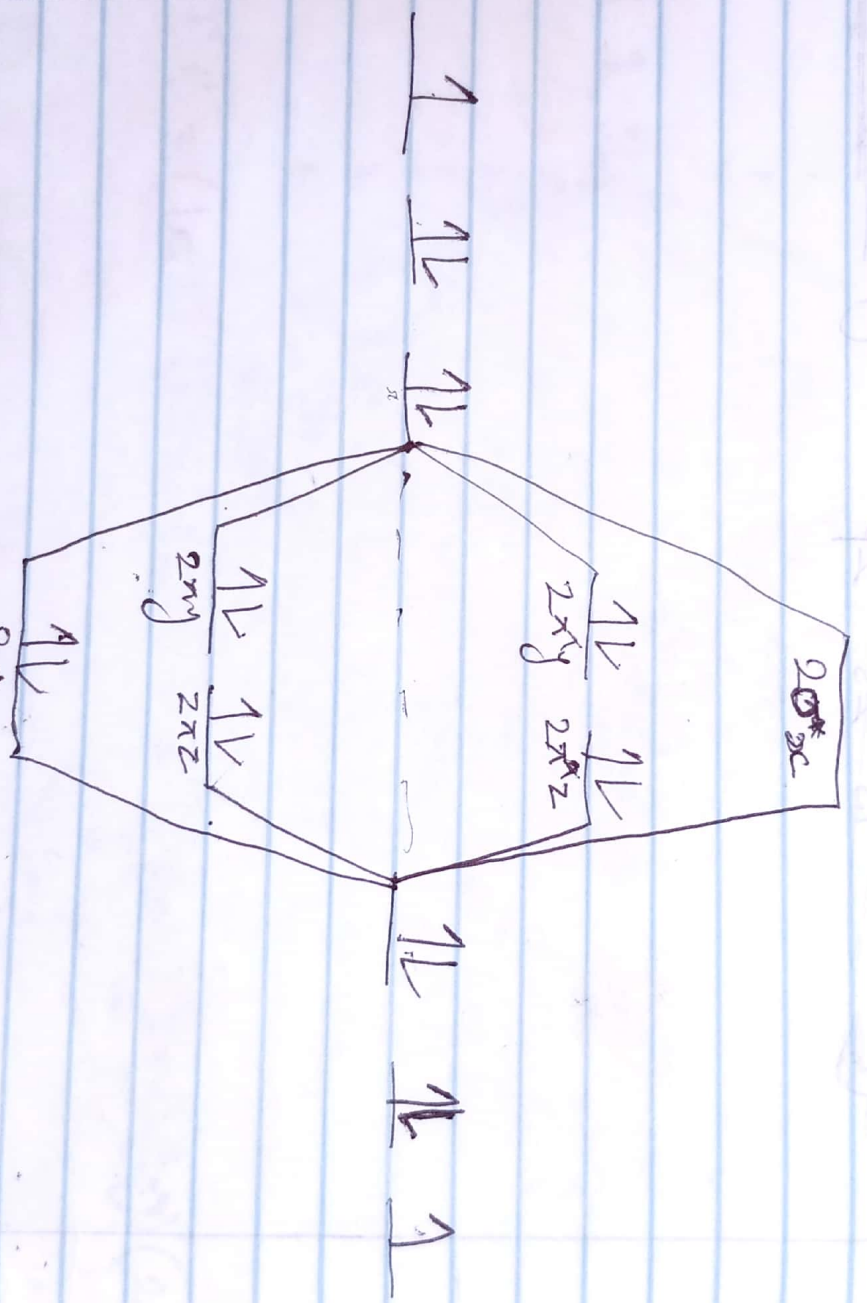


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Fluorine F_2

$F \rightarrow 1s^2 2s^2 2p^5$
 $F \rightarrow 1s^2 2s^2 2p^5$

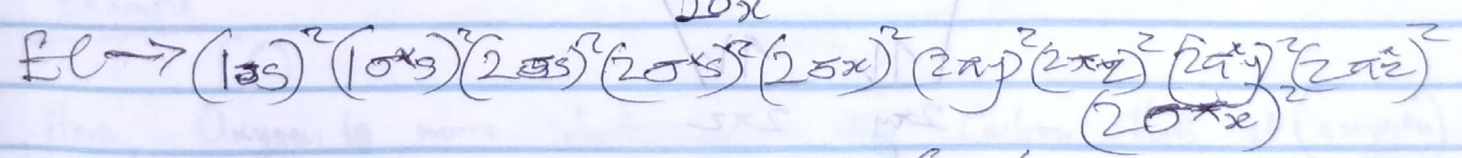
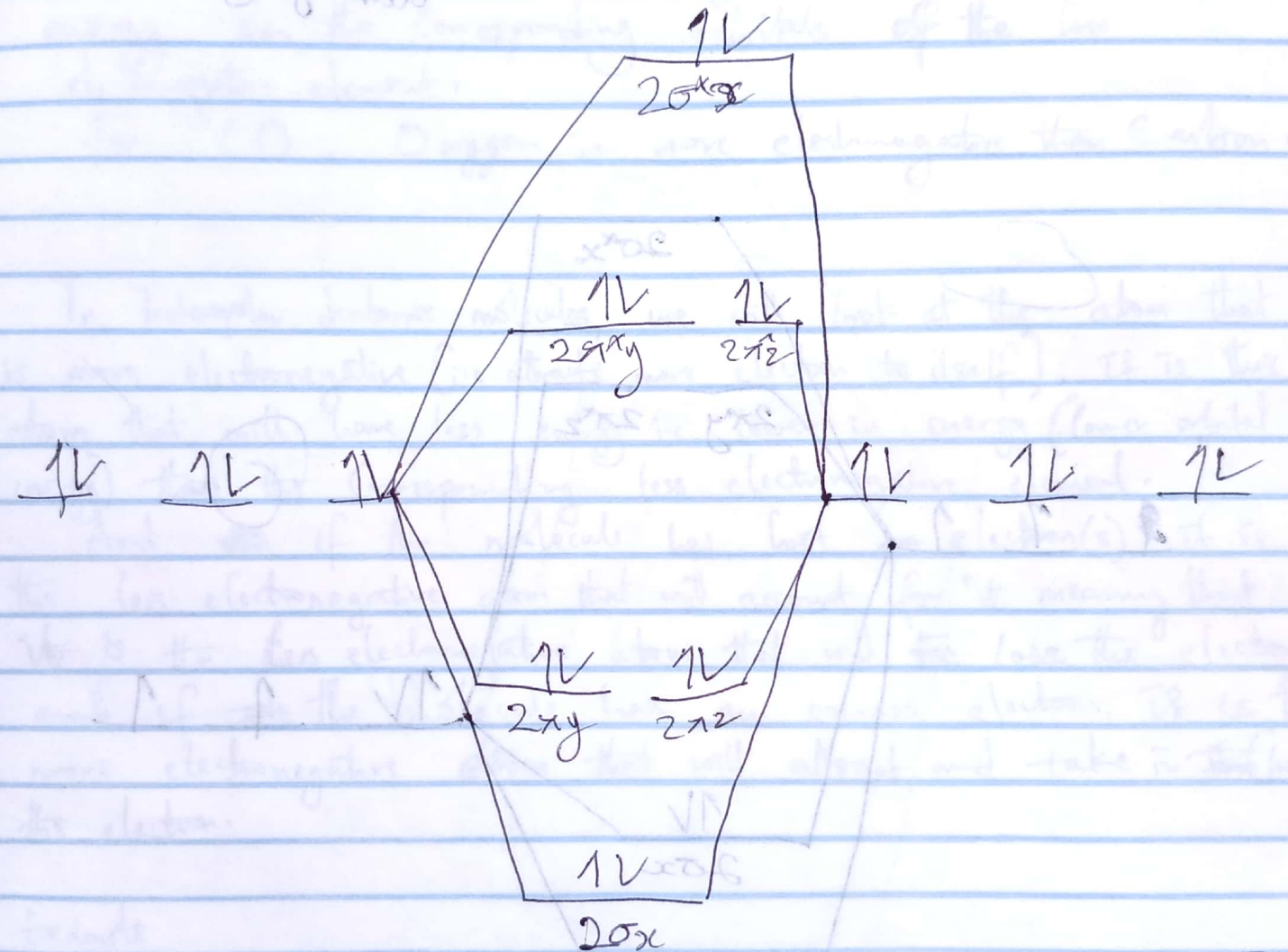
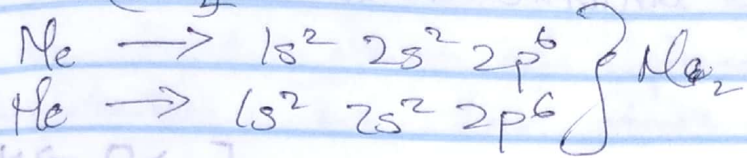
Molecular Orbital Diagram for F_2
 Atomic Orbitals: $1s, 2s, 2p_x, 2p_y, 2p_z$
 Molecular Orbitals: $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_z}, \pi_{2p_x}, \pi_{2p_y}, \sigma_{2p_z}^*, \pi_{2p_x}^*, \pi_{2p_y}^*, \sigma_{2p_z}^*$



$$FC = (1s)^2 (2s)^2 (2p_x)^2 (2p_y)^2 (2p_z)^2$$

Bond Order = $\frac{B.O - A.O}{2} = \frac{8 - 4}{2} = 2$

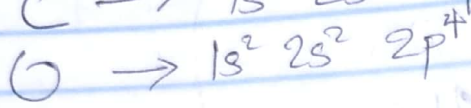
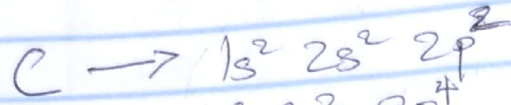
10. Neon (Ne)



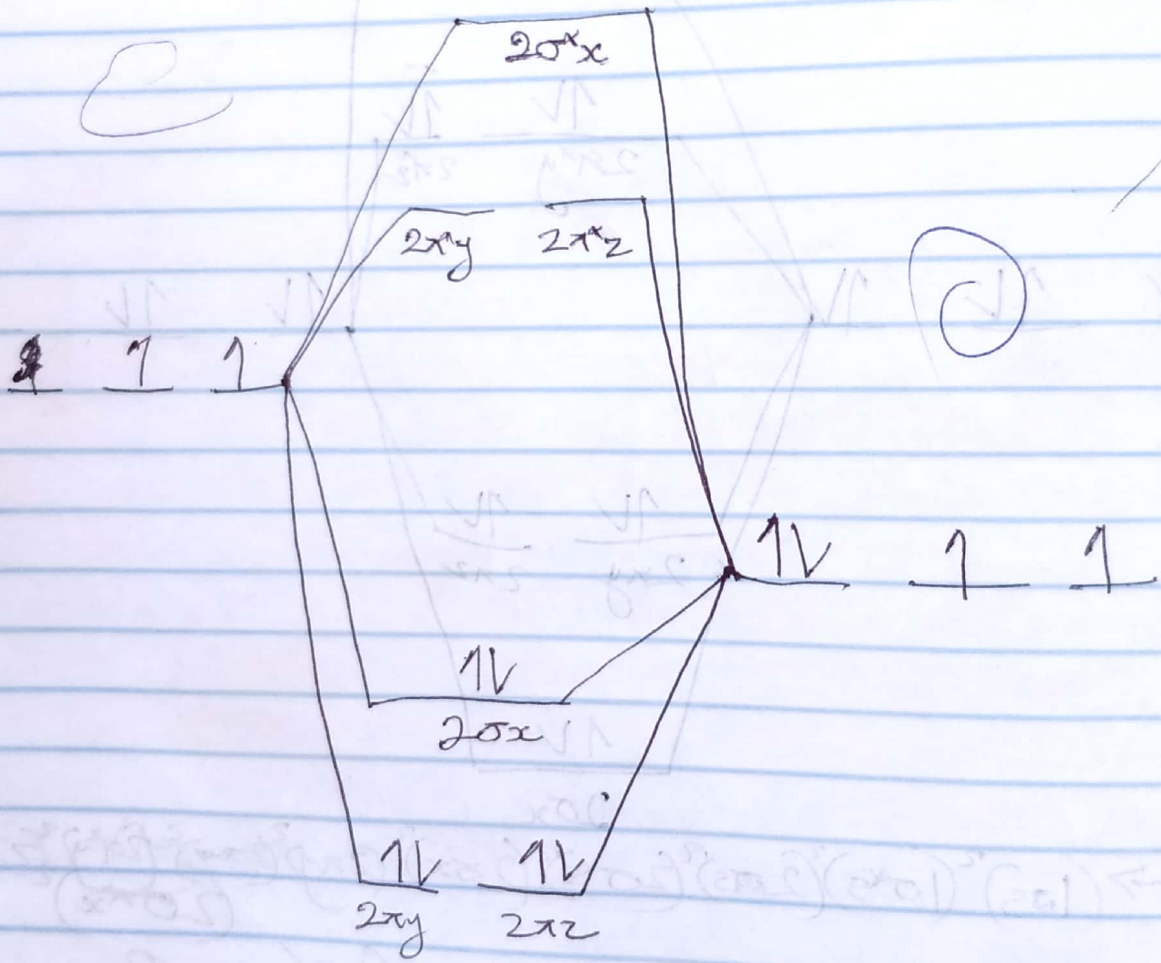
Bond order $\rightarrow \frac{8 - 4}{2} = \frac{4}{2} = 2$

HETEROPOLAR DIATOMIC MOLECULE

1. CO



F → O → N → C
 ↑
 Highest electronegativity



Note Heteropolar diatomic molecular energy diagram is always in the form above.

Heteropolar diatomic molecules are built from two different type of atoms. Atoms of different elements have different electronegativities; Thus, their atomic orbitals have different energies.

For Compounds like CO, NO and CN. The atomic orbital of the more electronegative element are lower in energy than the corresponding orbitals of the less electronegative element.

For CO, Oxygen is more electronegative than Carbon.

In heteropolar diatomic molecules, we will look at the atom that is more electronegative (i.e. attracts more electron to itself). It is this atom that will have less energy i.e. lower in energy (lower orbital energy) than the corresponding less electronegative element.

And, ~~the~~ if the molecule has lost ~~a~~ electron(s), it is the less electronegative atom that will account for it meaning that ~~it~~ is the less electronegative atom that will ~~lose~~ lose the electron and if ~~the~~ the molecule has an excess electron, it is the more electronegative atom that will attract and take in ~~the~~ (house) the electron.

Example

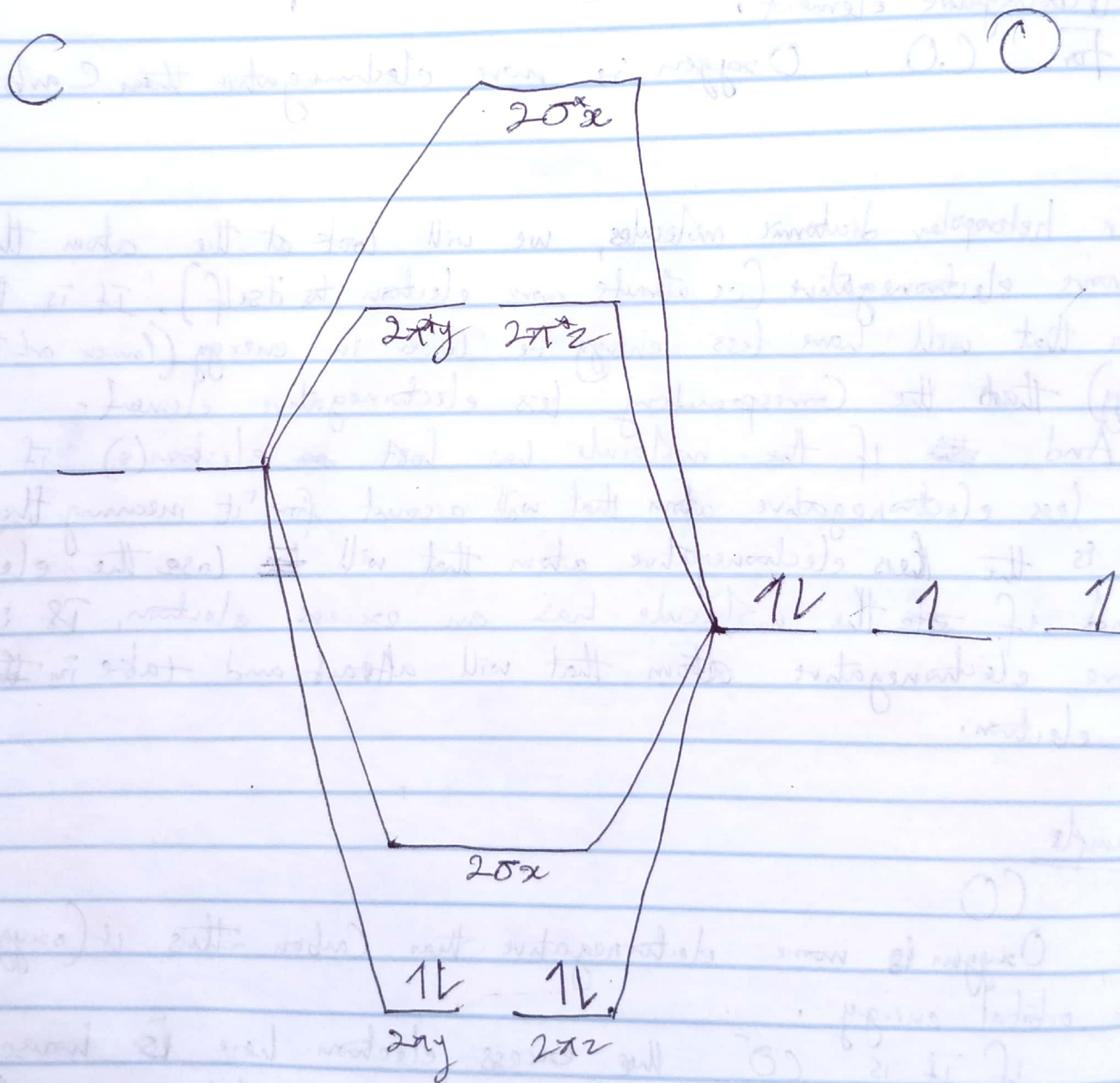
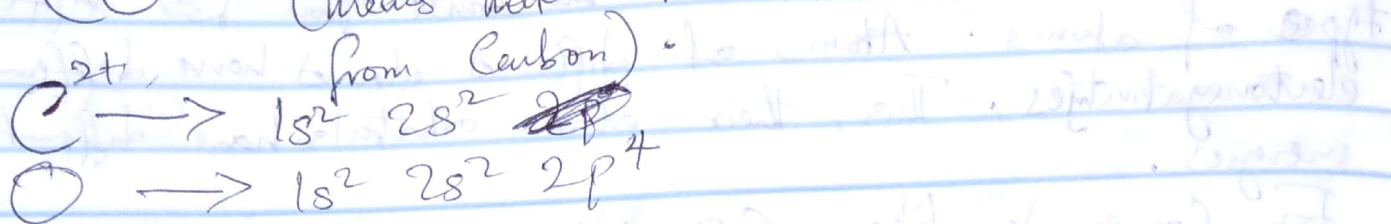
CO

Here, Oxygen is more electronegative than Carbon thus it (oxygen) has lower orbital energy.

If it is CO^- , the excess electron here is housed by Oxygen since it is more electronegative (attract electron to itself)

If it is CO^+ , the electron lost here will be from the Carbon atom since the oxygen is more electronegative (attract electron to itself) and Carbon is less electronegative (more electropositive than Oxygen) i.e. Carbon will lose the electron.

②. CO^{2+} (means that two electrons has been lost



OVERLAP OF ORBITALS

Overlap of Orbitals

Overlap of orbitals occurs when two orbitals of 2 atoms approach each other closely enough that they have sufficient amplitude in the region of space common to both of them. The resulting overlap may be positive, negative or zero, this depends on the nature of the orbitals that are involved in the overlap. Positive overlap results when the concerned orbitals have the same sign, this may be positive or negative.

Negative overlap results when the orbitals concerned have the opposite signs i.e. + combined with -

Zero overlap is a consequence of two opposite orbitals involved having precisely equal ratios of overlap with opposite sign.

To validate the above stated cases, if you consider two orbitals ϕ_1 and ϕ_2 which have positive overlap, the electron density is higher than the mere sum of the electron densities of the two separate orbitals.

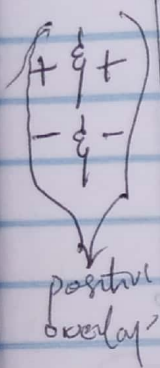
$$(\phi_1 + \phi_2)^2 > \phi_1^2 + \phi_2^2$$

And the difference is $+ 2\phi_1\phi_2$.

The attraction of both nuclei for this electron is greater than the mutual repulsion of the nuclei. A net force of attraction or bonding interaction therefore results. (The excess $2\phi_1\phi_2$ brings about bonding interaction)

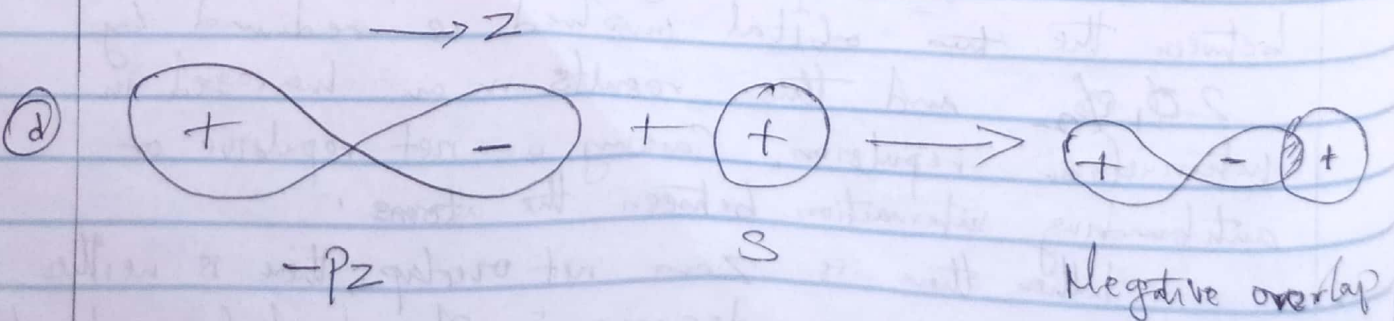
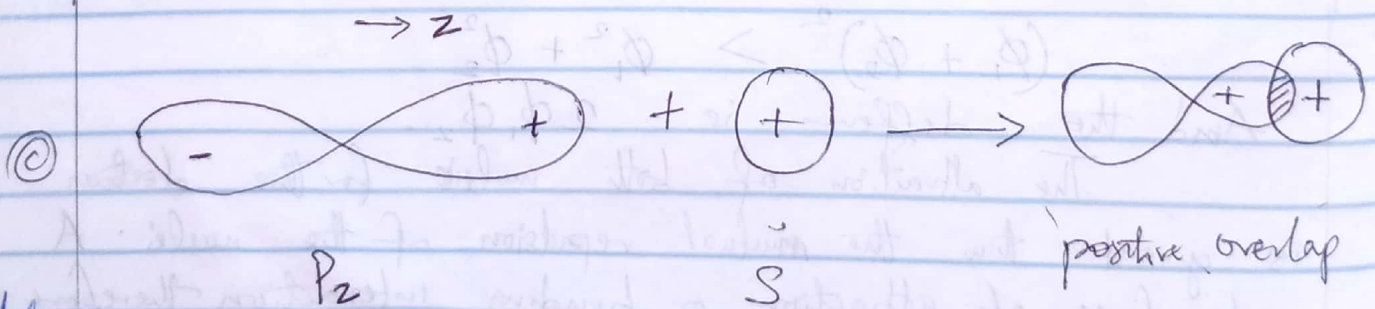
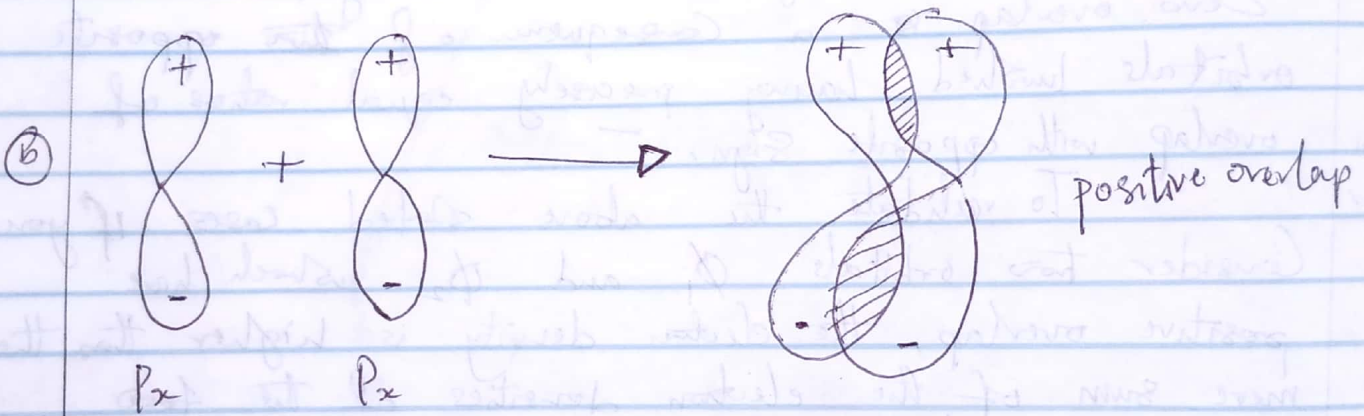
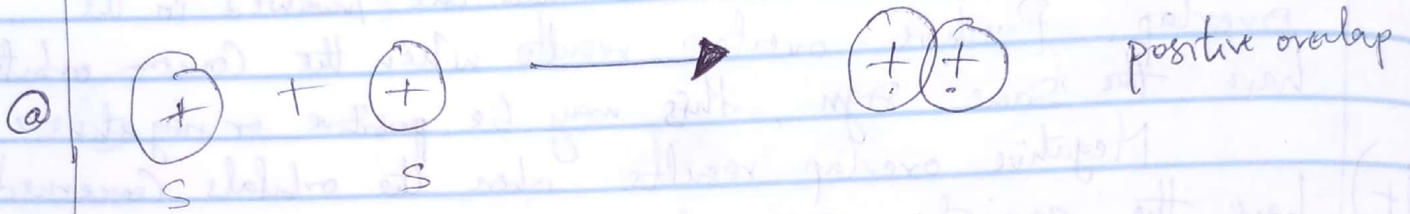
In the case of negative overlap, electron density between the two orbitals involved is reduced by $2\phi_1\phi_2$ and this results in an increased internuclear repulsion, causing a net repulsive or antibonding interaction between the atoms.

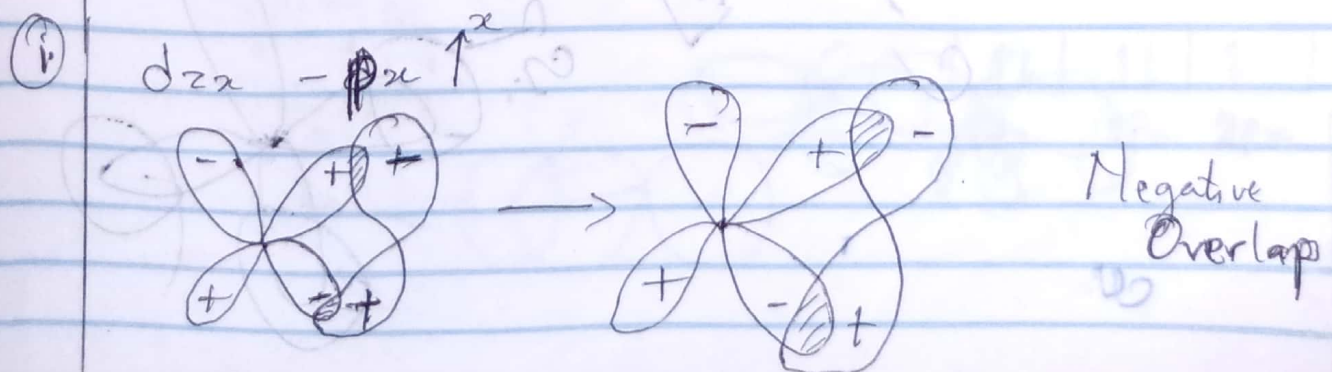
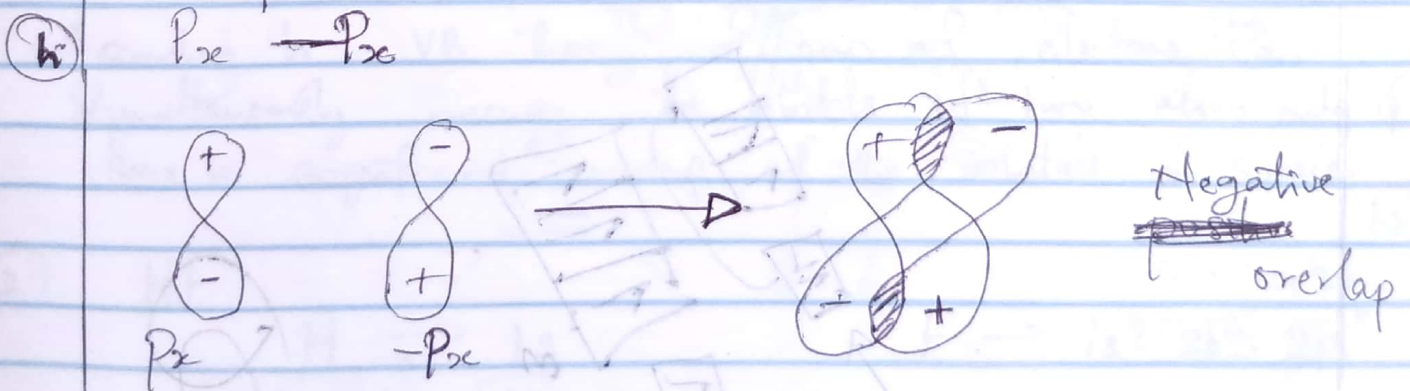
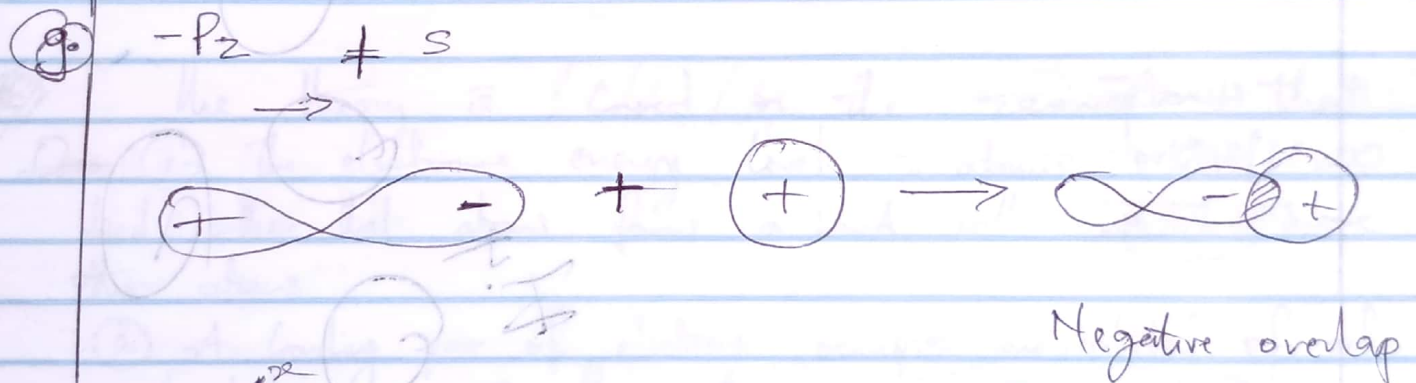
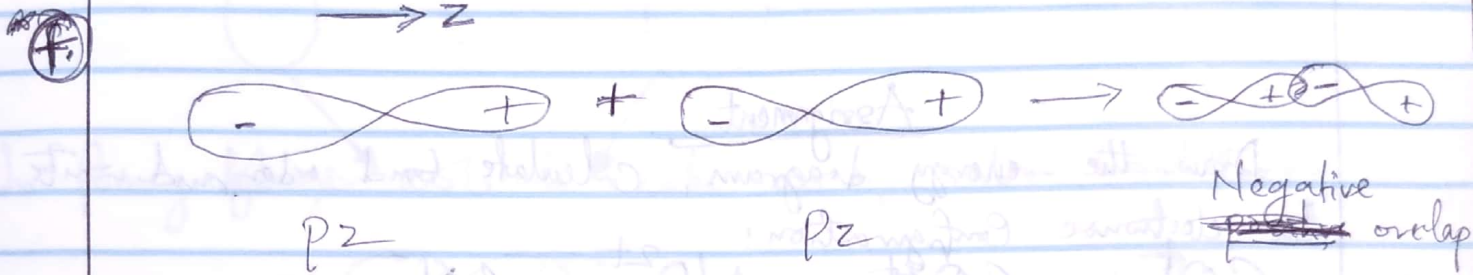
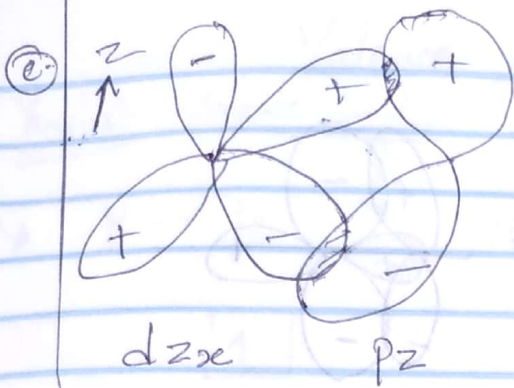
When there is zero net overlap, there is neither increase nor a decrease in shared electron density and consequently, neither a repulsive nor an attractive



Interaction result. This situation is describe as non-bonding.

Positive overlap

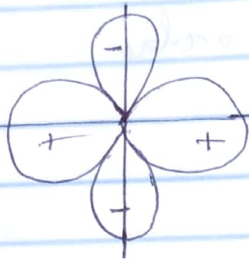




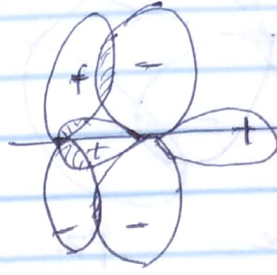
Zero Overlap



P_y

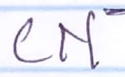
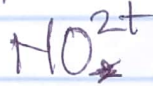
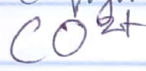
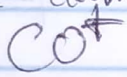


$d_{x^2-y^2}$

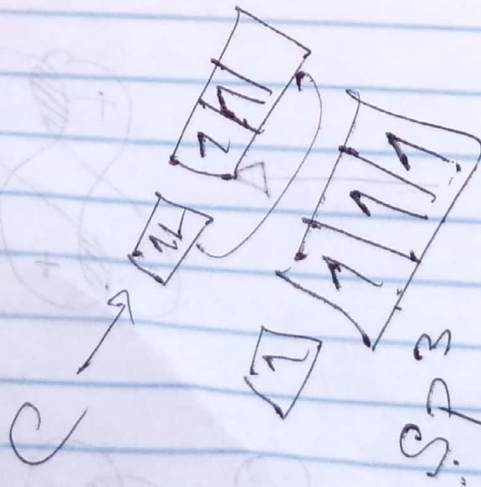


Assignment

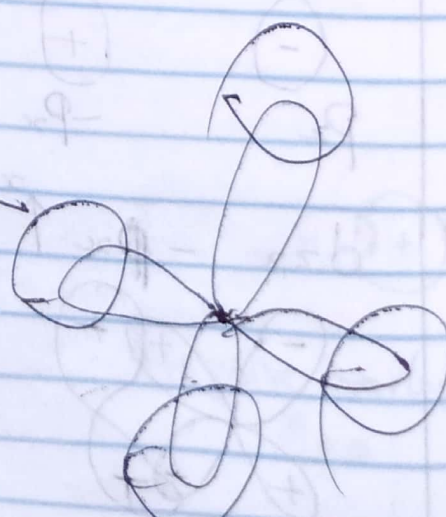
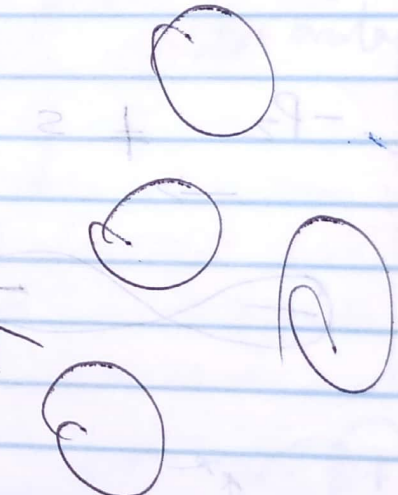
Draw the energy diagram, calculate bond order and write the electronic configuration.



H_{4-1}

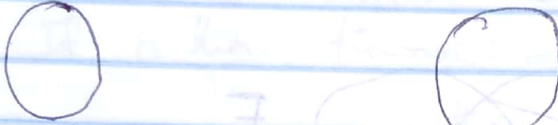
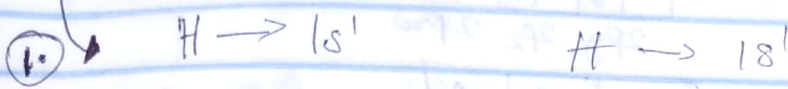


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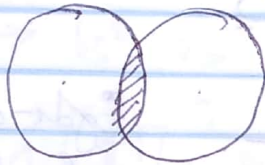


Valence bond Theory

Simplest valence bond



In forming hydrogen molecule make use of valence bond theory



sigma bond

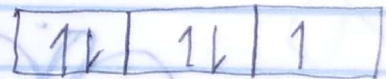
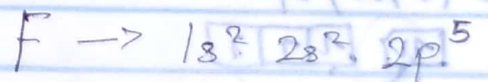
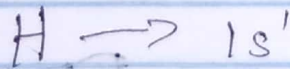
The theory is based on the assumptions that

- ① The electronic energy level in atomic orbitals are used when two atoms form a bond with one or more other atoms

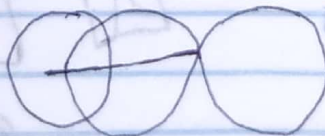
- ② A bonding pair of electrons occupies an orbital of each bonded atom simultaneously.

According to VB theory a pair of electrons can simultaneously occupy the orbitals of two atoms only if there is significant overlap of the orbitals in space.

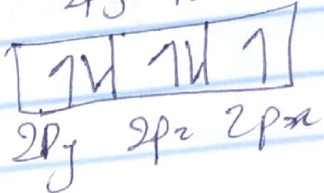
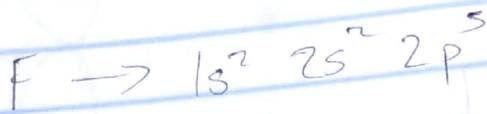
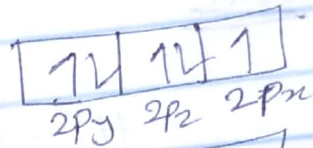
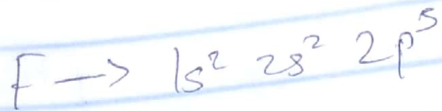
② HF



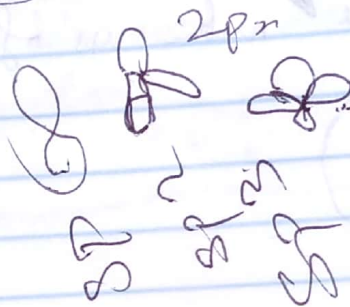
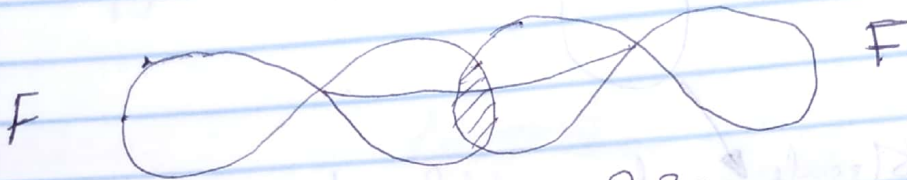
$2p_y$ $2p_z$ $2p_x$



③ F_2

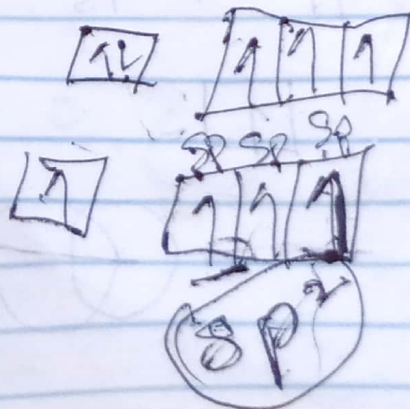
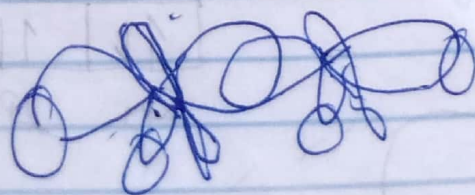
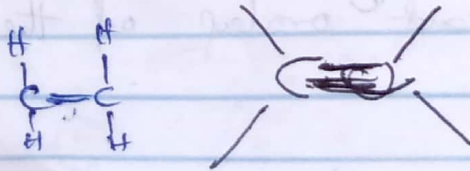
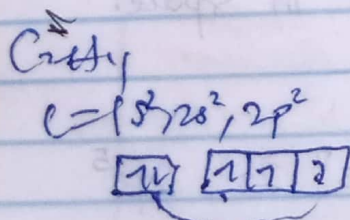
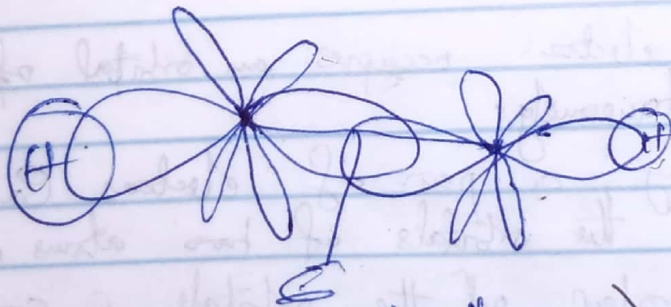
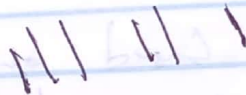
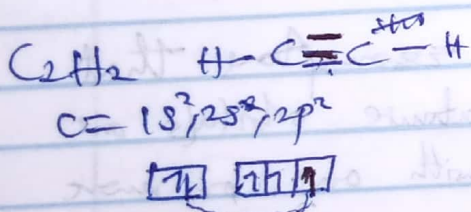


σ bond



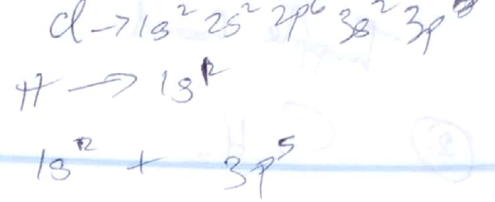
Edge-on overlap of orbital is sigma.

Side way overlap of orbital is pi.



3.3

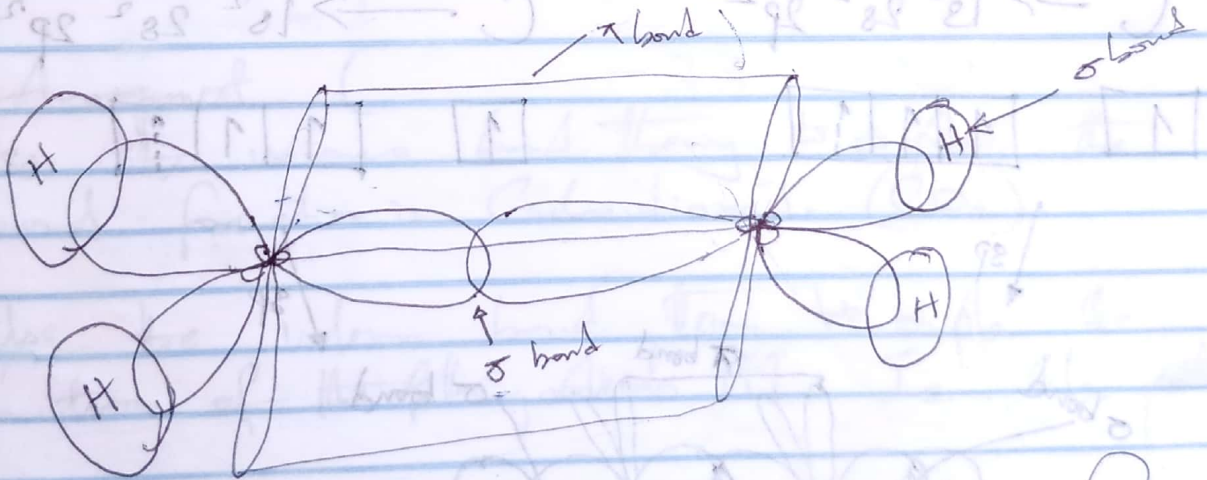
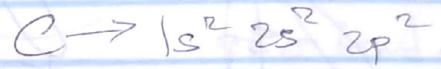
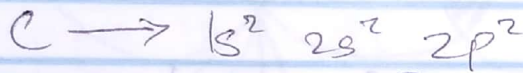
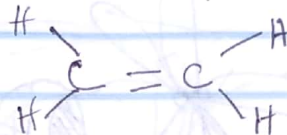
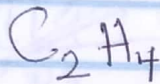
Double & Triple bonding



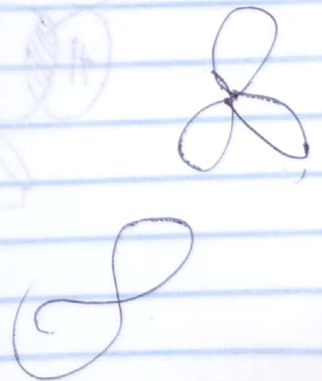
Multiple bonding

Two ~~sp~~ orbitals can also overlap each other side-by-side. When this happens, the resulting bond does ~~not~~ have axial symmetry. It is then known as pi (π) bond.

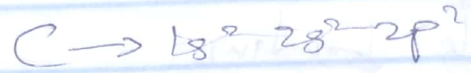
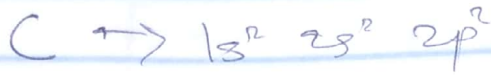
Example



A σ bond
 A π bond

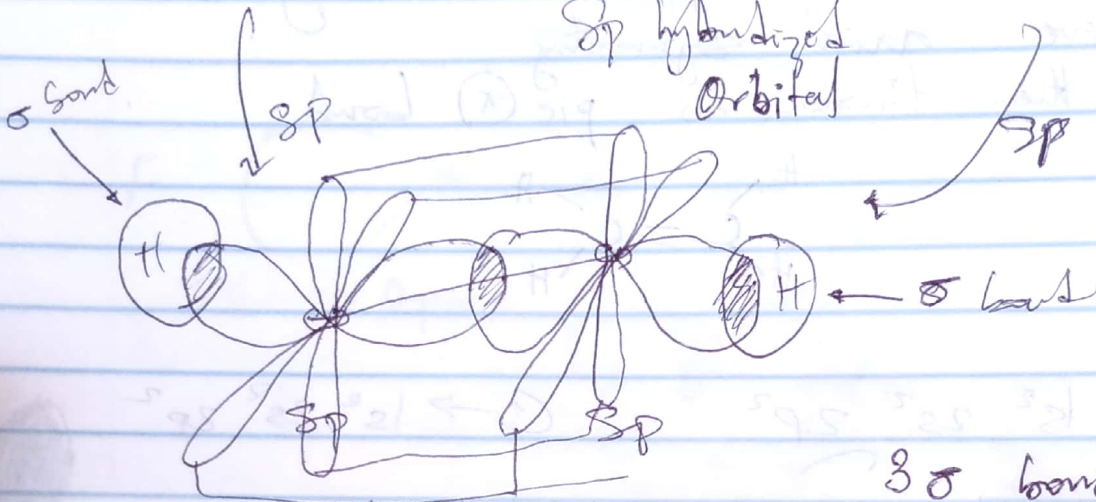


Triple bond



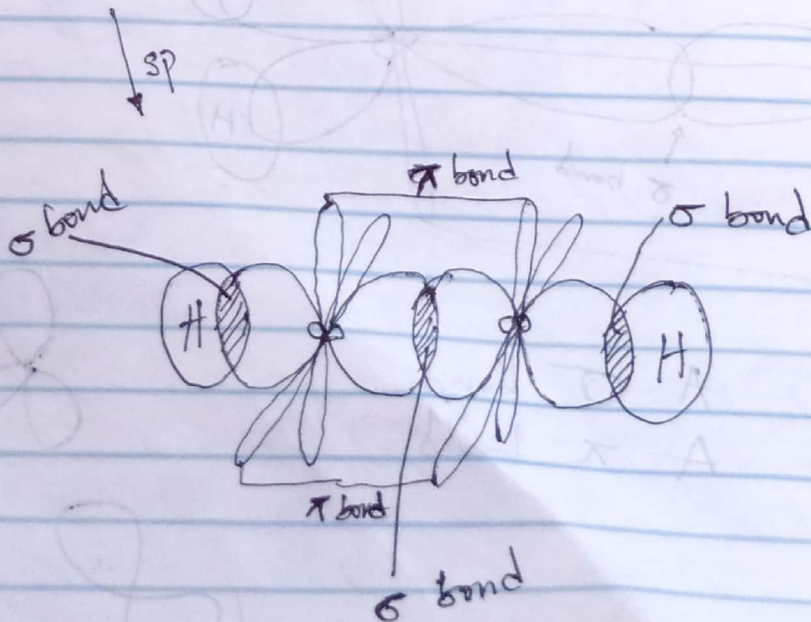
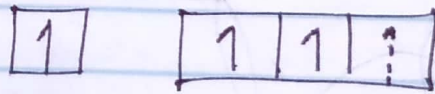
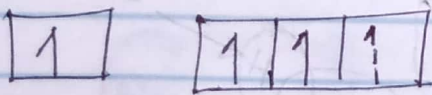
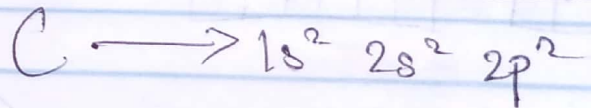
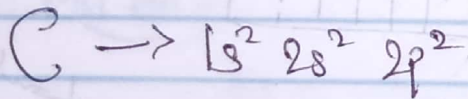
↑
excited state

sp hybridized orbital



3 σ bond
2 π bond

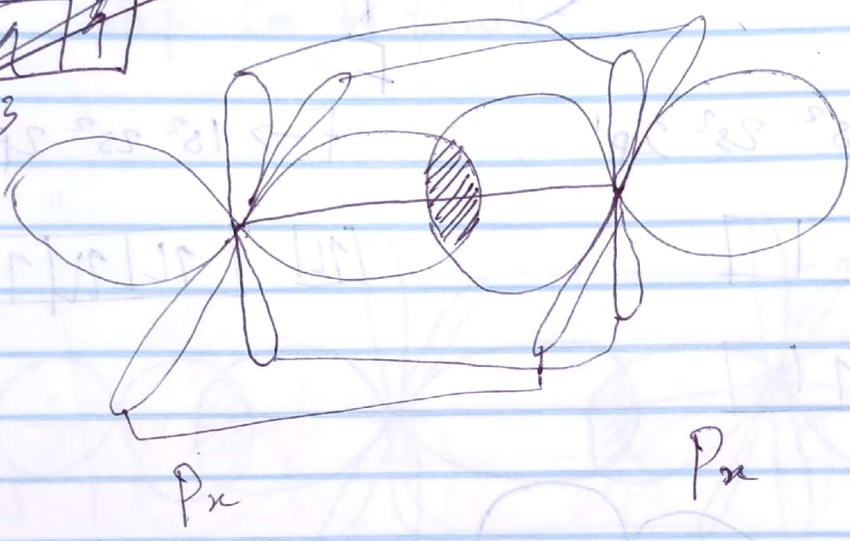
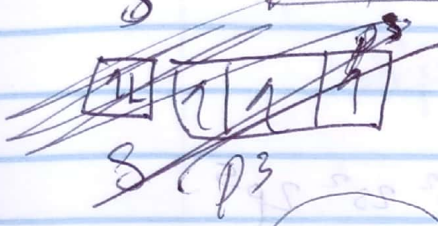
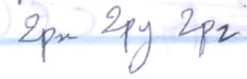
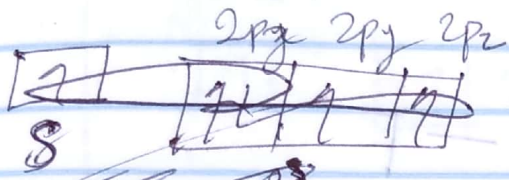
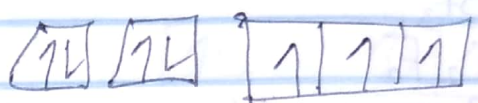
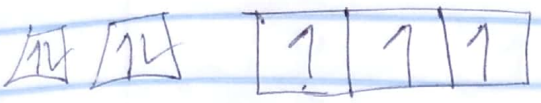
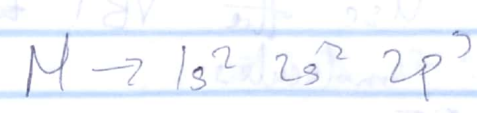
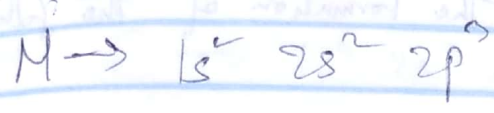
3 σ bond
2 π bond



3 σ bond
2 π bond

Triple bond

3. N_2



1 σ bond.
2 π bond.

Assignment (

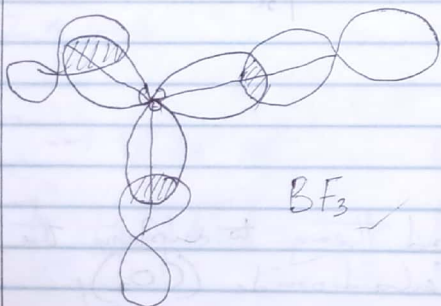
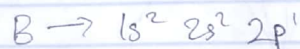
1. Use the valence bond theory to explain the bond formation in Carbondioxide (CO_2)
2. Use the valence bond theory to explain the formation of the following molecules HI , I_2 , Cl_2

10/7/2019

Use the VBT to explain the formation of the following molecules

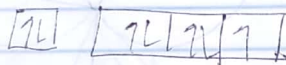
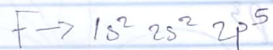
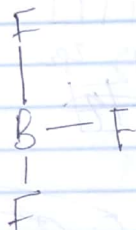
BF₃
C₂F₂
~~C₂F₄~~ CCl₄

⊙ BF₃

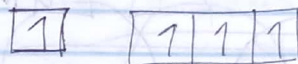
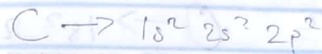


BF₃

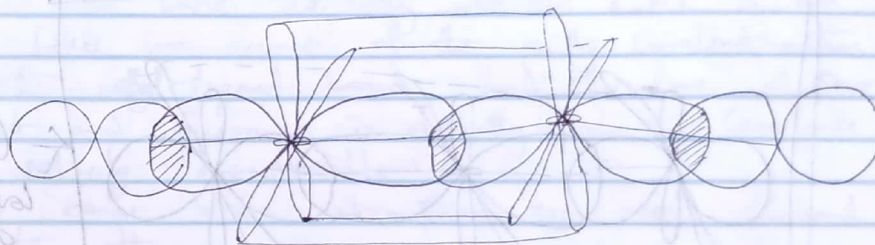
3 σ bonds



⊙ C₂F₂

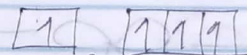
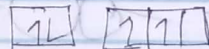
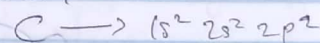


sp can be formed

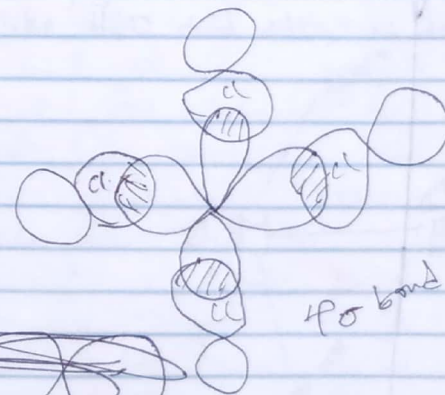


3 σ bond
2 π bond

⊙ CCl₄



sp³



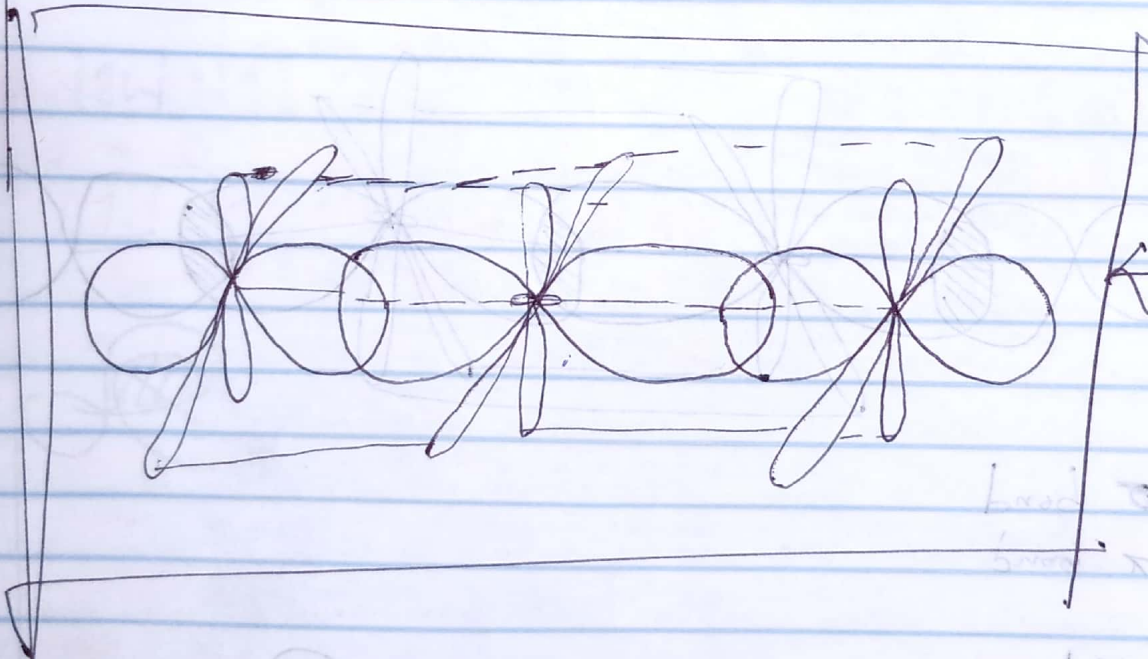
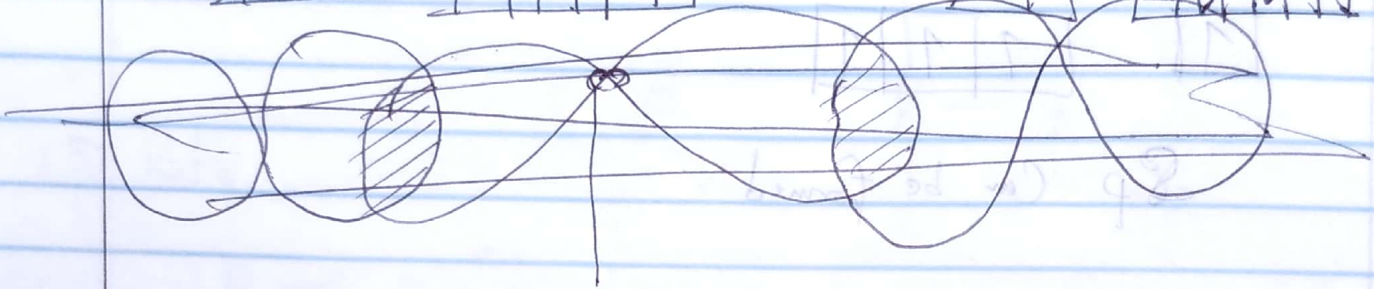
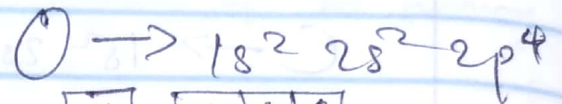
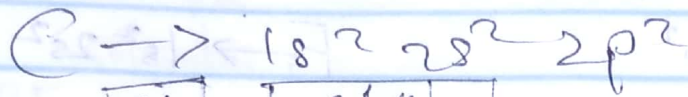
4 σ bond

sp³ hybridized
Carbon orbital
bond angle = 109.5°

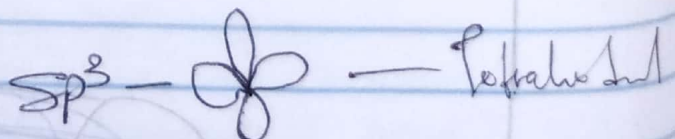
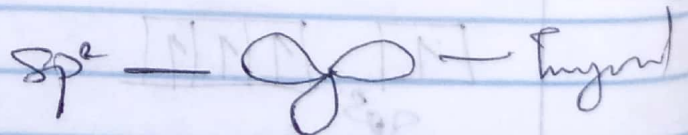
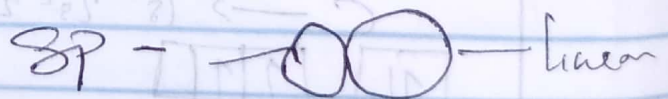


$sp^3 \rightarrow$ Linear
 $sp^2 \rightarrow$ Trigonal
 $sp^3 \rightarrow$ Tetrahedral

d. CO_2



Correct by Dean.



01/04/19

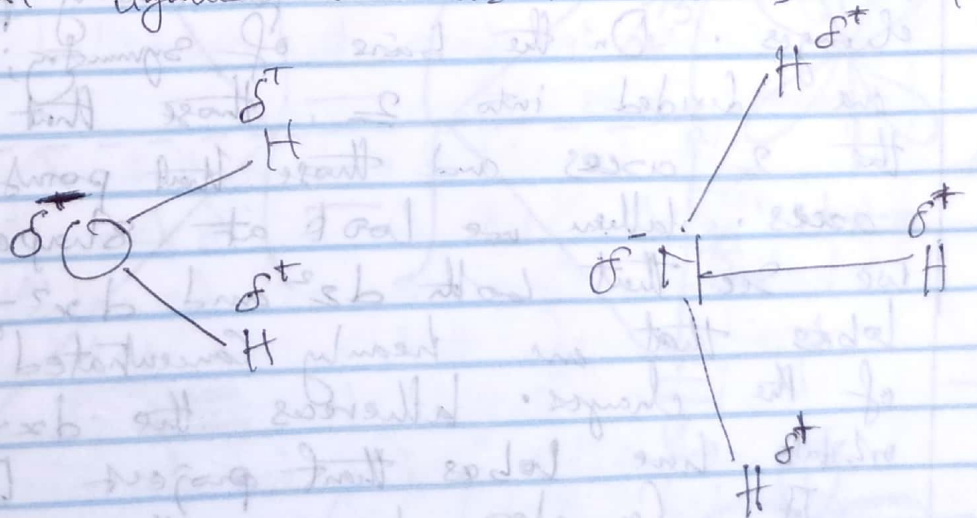
CRYSTAL FIELD THEORY

The crystal field theory is essentially the application of ionic bond theory to metal complexes. Crystal field theory provides a very simple and easy way of ~~putting~~ ~~fitting~~ treating numerically many aspects of the electronic structures of complexes. It successfully accounted for colours and magnetic properties of hydrated salt of transition metals. It is also used to interpret electronic spectra - and ^{partly} explaining properties of metal-2⁺ and metal-3⁺ ions of the first transition series.

The basic difficulty with the CFT is that it takes no account of the partly covalent nature of the metal-ligand bond and therefore whatever effects and phenomena is due to the covalence are entirely inexplicable.

Some basic assumptions are put forward in this theory:

1. It takes the ligand as point chargeless - charges like ligand such as F^- , Cl^- and I^- are regarded as point charges without physical dimensions and also takes neutral ligands like H_2O and NH_3 as dipoles



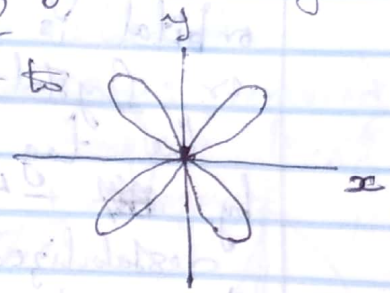
2. The central atom carries a positive charge.
3. It totally neglects the possibility of overlap of the ligands and central metal ions.
4. A purely electrostatic interaction is assumed for the ligand and the metal ion.

The splitting of the d-orbitals by electrostatic field. If you

consider metal ion (M^{n+}) lying at the center of an octahedral set of point charges.

Suppose that this metal ion has a single d-electron outside of closed shell. e.g. Ti^{3+} . When it is in free state, this d-electron will have equal chance of being in any of the 5-d-orbitals (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{z^2}) because they are equivalent but the d-orbitals are not all equivalent, some are concentrated in the region of space close to the negative ion than other ones. The electrons prefer to stay in the orbital that is far away from the negative charges. On the basis of symmetry, the d-orbitals are divided into 2, those that point towards the z-axis and those that point in-between the axes. When we look at shape of d-orbitals we see that both d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that are heavily concentrated in the vicinity of the charges. Whereas the d_{xy} , d_{yz} and d_{xz} orbitals have lobes that project between the charges. It can also be seen that each of the 3 orbitals (d_{xy} , d_{yz} , d_{xz}) is equally favorable for the electron. These 3 orbitals have entirely equivalent environment in octahedral complex.

* In the Octahedral environment of 6 negative charges the metal ion now has 2 kinds of d-orbitals, 3 of one kind equivalent to one another and conventionally labelled t_{2g} (d_{xy} , d_{yz} , d_{zx}) and 2 of another kind equivalent to each other conventionally labelled e_g ($d_{x^2-y^2}$, d_{z^2})

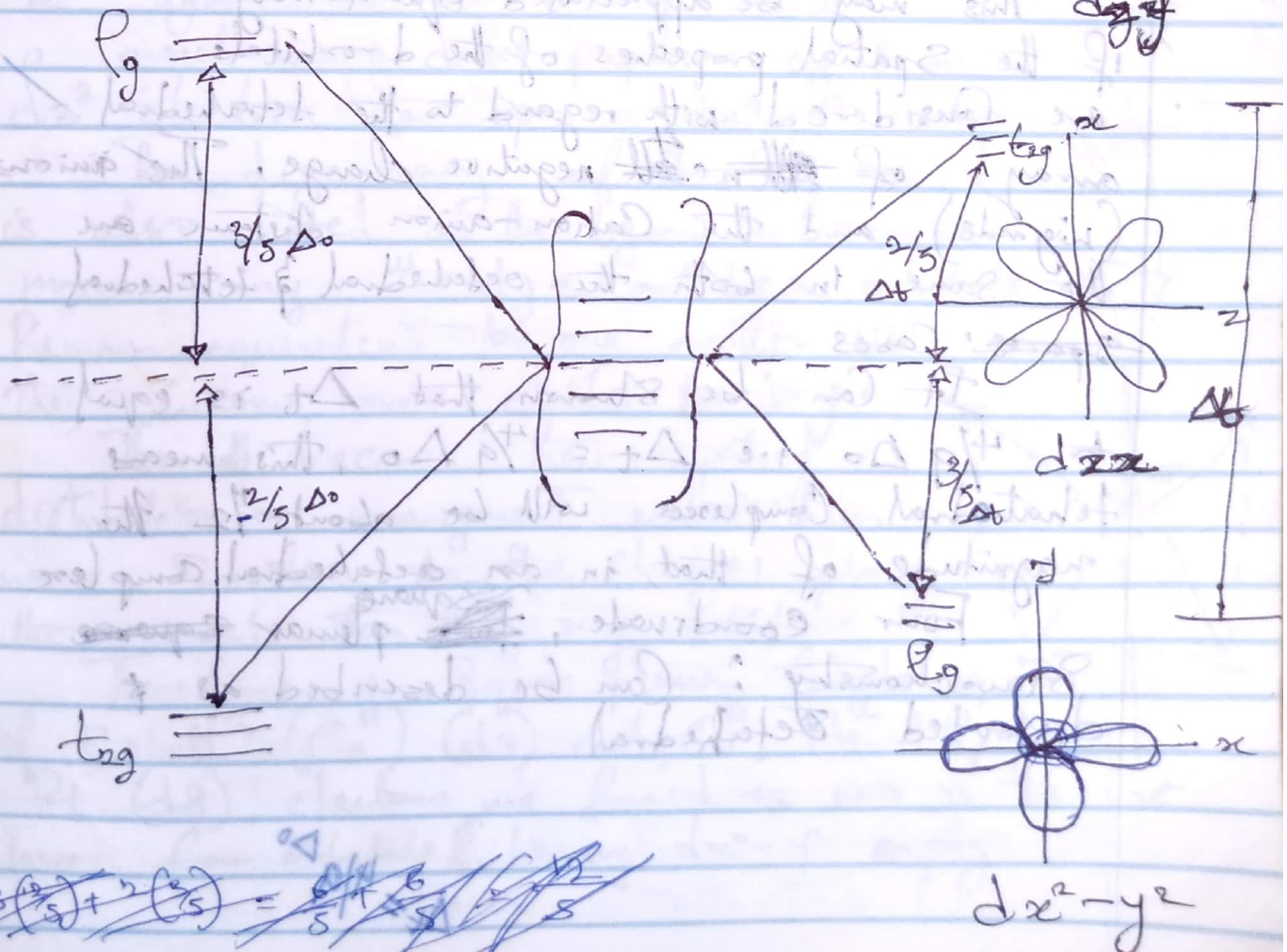
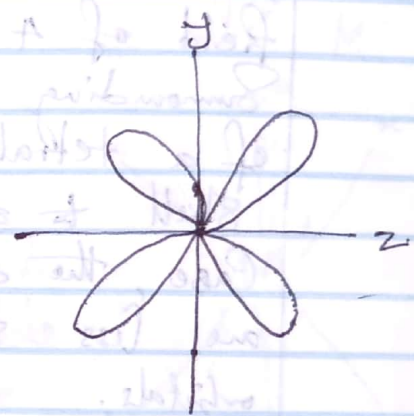


The e_g -orbitals are of higher energy than the t_{2g} orbitals.

e_g orbitals are of higher energy because they point directly at the ligands.

Since they lie on the axes and the three t_{2g} point between the axes

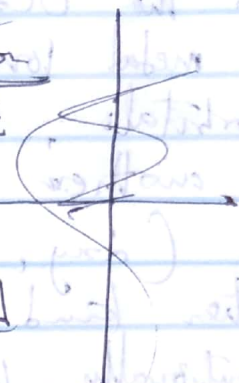
The next consequence is the splitting of the two orbitals into 2 sets



~~$3 \times \frac{2}{5} \Delta_o + 2 \times \frac{3}{5} \Delta_o = \frac{6}{5} \Delta_o + \frac{6}{5} \Delta_o = \frac{12}{5} \Delta_o$~~

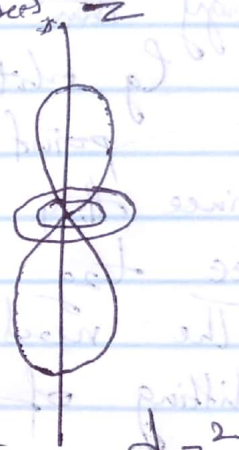
The energy difference between t_{2g} and e_g orbital is called the energy of separation or Crystal field Splitting energy, CFSE

The t_{2g} orbitals are stabilized by $-4\Delta_o$ while the e_g is destabilized by $6\Delta_o$. The observed physicochemical properties depend on this splitting of the crystal field.



* Considering a tetrahedral complex,

It can be shown that the electrostatic field of 4 charges in the octahedron surrounding an ion at the vertices of a tetrahedron causes the shell to split up. In this case, the d_{xy} , d_{yz} & d_{zx} orbitals are less stable than the $d_{x^2-y^2}$ & d_{z^2} orbitals.



This may be appreciated quantitatively if the spatial properties of the d-orbitals are considered with regard to the tetrahedral array of ~~the~~ negative charge. The anions (ligands) and the cation-anion distance are the same in both the octahedral & tetrahedral cases.

It can be shown that Δ_t is equal to $4/9 \Delta_o$ i.e. $\Delta_t = 4/9 \Delta_o$, this means tetrahedral complexes will be about $1/2$ the magnitude of that, in an octahedral complex.

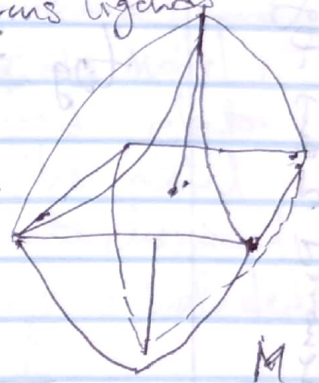
Four coordinate, ~~square~~ ^{square} planar ~~square~~ ^{square} geometry can be described as a distorted tetrahedron.

$4/9 \Delta_o$

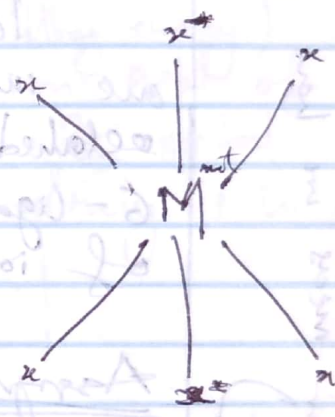


* Four Co-ordinate, Square planar Stereochemistry can be described as distorted octahedral with two trans ligands on the z-axis removed.

If you consider an octahedral complex MX_6 from which we slowly withdraw 2-trans ligands and let the two ligands be on the z-axis. As soon as the distance from M^{+n} to these two ligands become greater than the distance to the other four, new energy differences among the d-orbitals arise, then degeneracy (lifting of the degeneracy) of the d_{xy} orbital is lifted (One of d_{z^2} , $d_{x^2-y^2}$ is drawn therefore they don't have equal energy again).

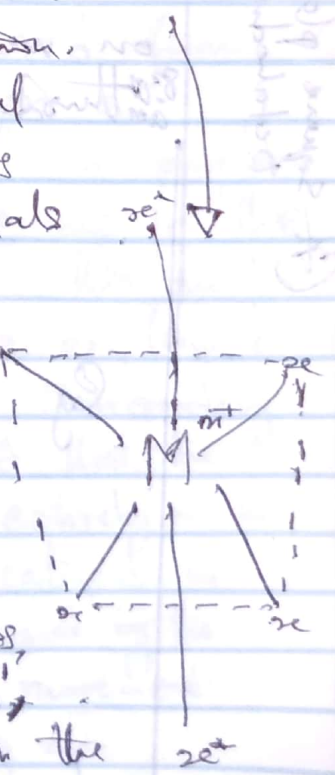


This d_{z^2} orbital become more stable than the $d_{x^2-y^2}$, this happens because the ligands on the z-axis exert a much more direct repulsive effect on a d_{z^2} electron than upon a $d_{x^2-y^2}$ electron.



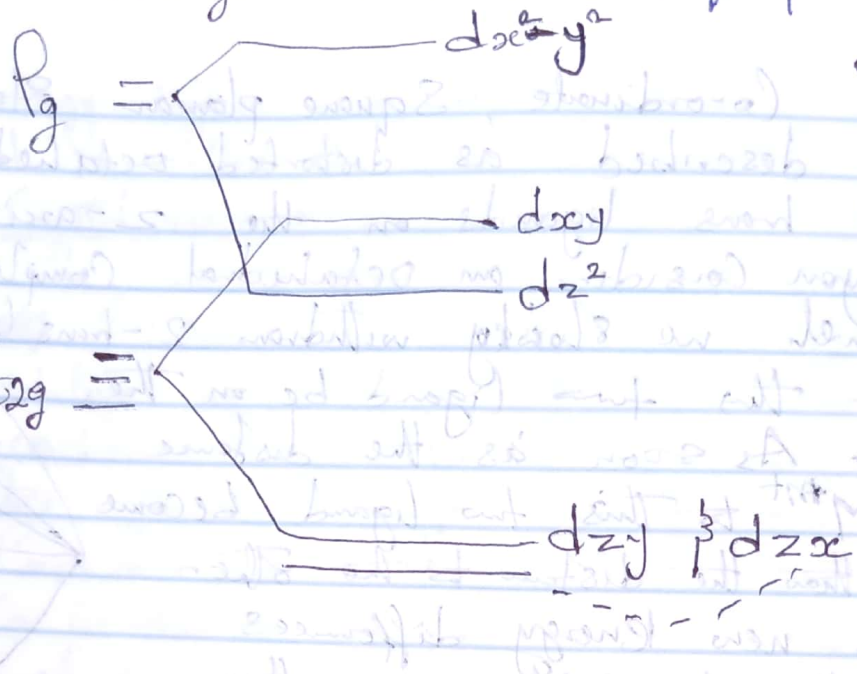
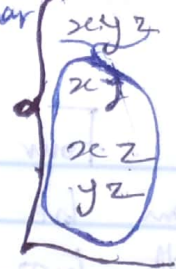
The degeneracy of the t_{2g} orbital is also lifted as the ligands on z-axis move away, the d_{yz} and d_{zxc} orbitals remain equivalent to one another but they become more stable than d_{xy} .

The d_{xy} because their spatial distribution or arrangement makes them more sensitive to the charges along the z-axis than the d_{xy} orbital.



Therefore, in square planar complexes of Co^{2+} (Co^{II}) (d^7) and Cu^{2+} , Ni^{2+} , Pb^{II} , Pt^{II} (d^8), electrons are forced to pair in the lower four orbitals leaving $d_{x^2-y^2}$ empty.

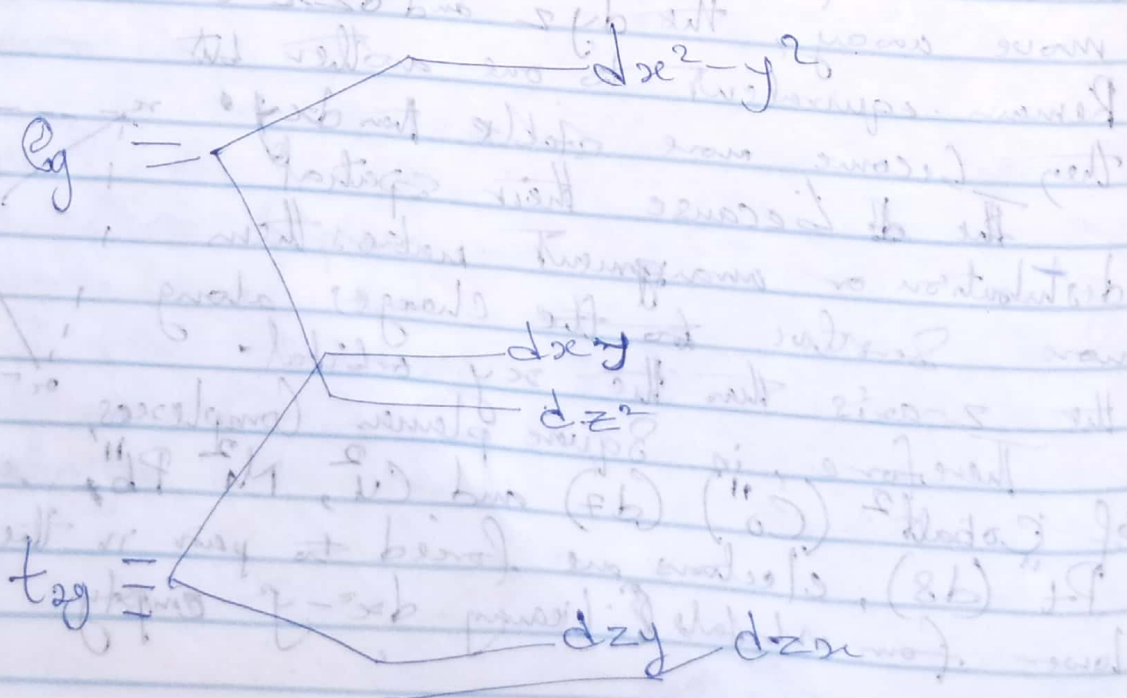
Arrangement in Octahedral Square planar



Tetragonally distorted octahedral complexes are intermediate between square planar and octahedral extremes and they arise because the 6-ligands are not identical or as a result of ions outside the coordination spheres.

Assignment of Read, understand & do Explain Jahn Teller ~~equation~~ effect on metal complexes formation to be submitted on am thursday.

A square planar means we have removed 2 ligands from the Octahedron.



CFT failed to explain some observations on need for further

Adjusted Crystal field Theory

There are evidences from ESR and NMR (Electron spin resonance & nuclear magnetic resonance) to support the essential role of Covalency in coordinate bonding despite the huge success of the Crystal field Model.

This shows that appreciable unpaired electron density lies on the ligand and not the metal and the ~~other~~ Order of ligands in Spectrochemical Series can only be explained if Covalency is included among the other factors.

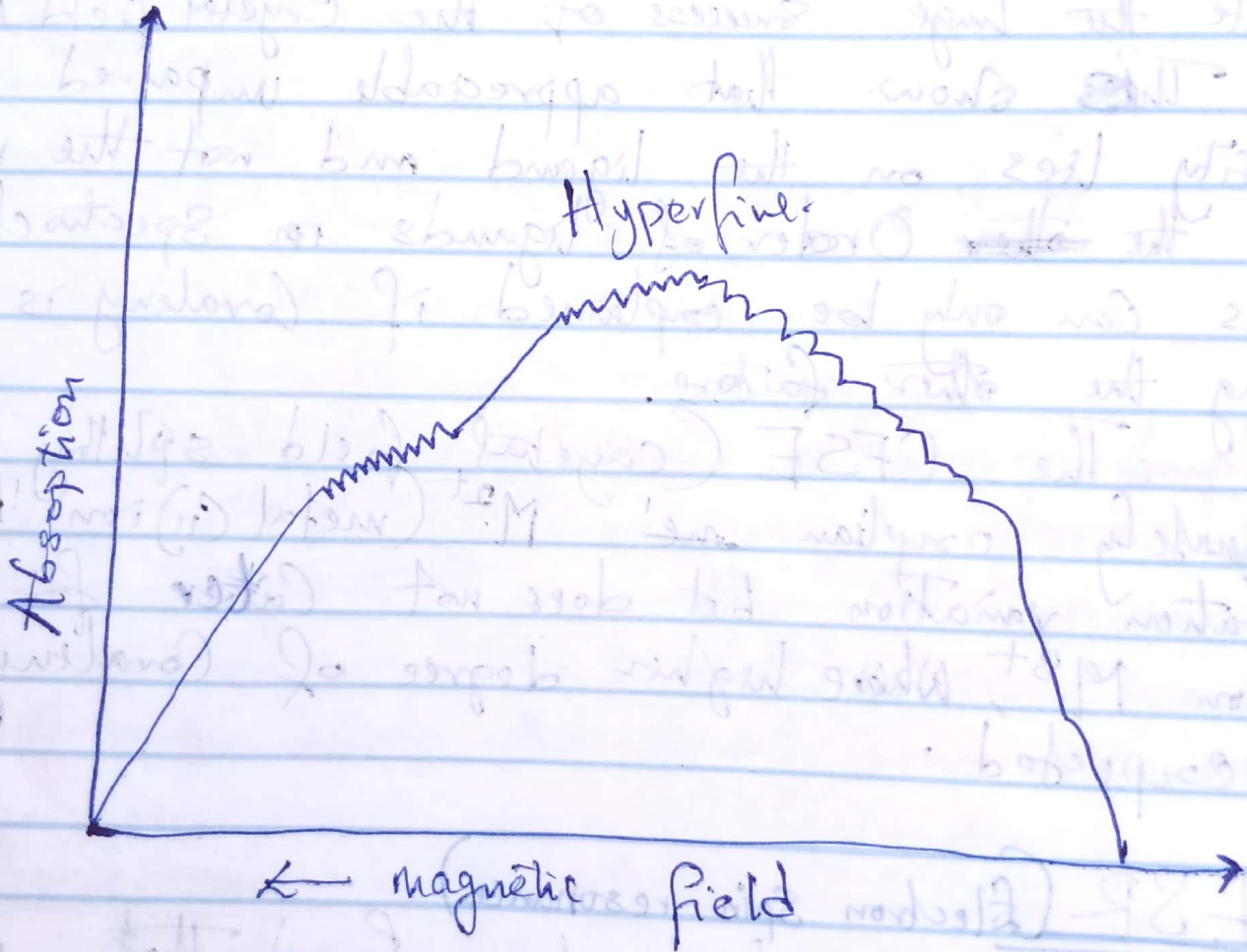
The CFSE (Crystal field splitting energy) adequately explain the M^{2+} (metal (ii) ion) heat of hydration variation but does not cater for metal (iii) ion M^{3+} , where higher degree of Covalency is to be expected.

ESR (Electron Spin Resonance)

In many cases, it has been found that instead of the single absorption band expected from the group of d-electron localised on a particular metal atom, there is observed a complex pattern of ~~substance~~ ~~sub-~~ sub-bands as in the case of Iridium tetrachloride ion ($IrCl_6^{2-}$). This sub-band

called the hyperfine structure is explained by assuming that certain orbital of the surrounding chloride ion overlap to such an extent that the single unpaired electron is not localized entirely on the metal ion but ~~instead~~ it's about 5% localized on each chloride ion. The structure is also caused by the nuclear magnetic resonance movement of the chloride and the hyperfine splitting are ~~prop~~ proportional to the fractional extent to which the unpaired electron is only 75% Iridium (IV)

of ~~total~~ electron. Instead of 100% assumed by the purely electrostatic crystal field theory.



Question: Explain the cause of the high first ionization energy in noble gases.

Question by Dean
Note this points

Be informed that the hybridization state of Carbon in CH_4 , C_2H_4 and C_2H_2 is sp^3 , sp^2 and sp respectively and that H can be substituted for another atom and that still does not change the hybridization state of Carbon. Example CBr_4 would still be sp^3 and C_2Cl_4 would still be sp^2 .

Be informed that the only difference between CH_4 and CBr_4 is that in CBr_4 it is the p orbitals of Br that would overlap with the sp^3 Carbon atom and not s orbital like in the case of hydrogen in CH_4 .

Be informed that triple bond exists in C_2H_2 just like in C_2F_2 and that this triple bond is a result of one sigma bond and two other pi bonds resulting from unhybridized p_y and p_z orbitals.

Know that BeCl_2 is a linear molecule resulting from hybridized sp orbital of Be. Under hybridization, one of the electrons on the $2s^2$ orbitals is excited to a vacant p orbital, thereby giving room for the formation of an sp hybrid orbital with linear configuration.

① Using VBT, explain ~~C_2H_2~~ $\text{C}_2\text{F}_2\text{H}$

Questions

What is the total number of electrons in the antibonding orbital of CH^- ?

What is the difference between tetrahedral and square planar arrangement?

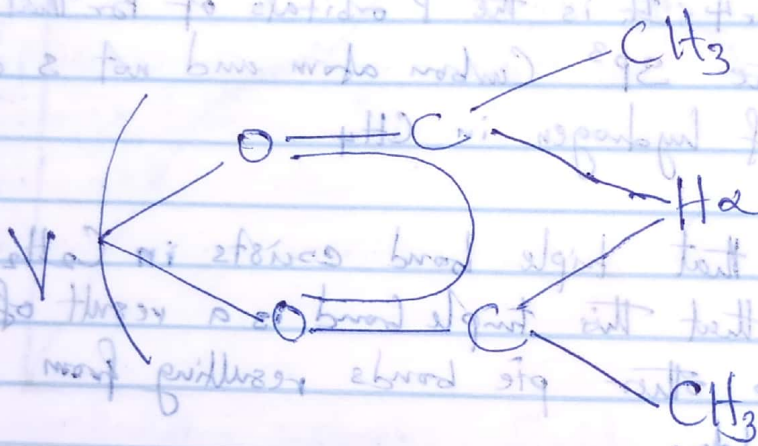
How can you explain some covalency in adjusted crystal field theory based on ESR and NMR.

NMR

Nuclear magnetic Resonance.

Nuclear resonances of atoms in ligands by unpaired electrons in the metal can be explained that there is transfer of electron spin density from metal orbital into orbitals of ligands atoms.

In this (Acetylacetonato) vanadium, the resonance frequency of $H\alpha$ result from transfer of spin density from metal to π -electron system and eventually to $1s$ orbital of hydrogen atom.



Intensities of $d-d$ transition

Another indication that metal ions and ligand orbitals overlap, with the result that d -orbitals of the metal ion are not pure metal-ion d -orbital is given by the intensities of the optical absorption bands due to $d-d$ transition.

If the crystal field approximation are perfect, the only mechanism by which this absorption could gain intensity would be by interaction of the d -orbital wave functions with vibrational wave function of the complex ion and by mixing of d -orbitals with other metal ion orbitals in these complexes (e.g. octahedral) where there is no centre of symmetry. There are however, cases in which it is clearly certain that this is a process.

are insufficient to account for the intensities observed and it must be assumed that the additional process of overlap and mixing of the metal d-orbitals with ligand atom orbitals, which is a powerful mechanism for enhancing the intensities occur to the significant degree.

16/04/2019

NEPHELAUXETIC EFFECT

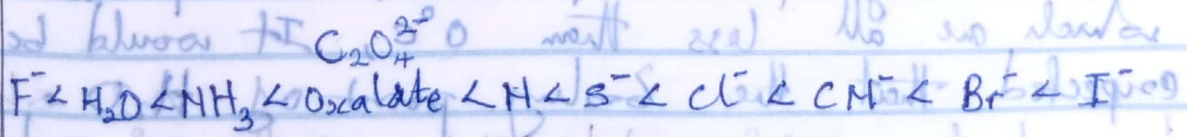
NEPHELAUXETIC EFFECT.

The effect of ligands on expanding d-electron cloud on the metal is known as Nephelauxetic effect.

It was assumed that separation between various R-S (Russel-Saunders) state are exactly the same in complex ion as in free gaseous ion but experimental data does not support this. It is found that decrease in energy separation is actually due to the d-electron cloud expansion in complexes, resulting in the increased mean distance between d-electron and the decreasing inter-electronic repulsion. This occurs partly because d-orbital overlap with ligands atomic orbitals and hence, d-electron can escape to some extent from the metal.

Nephelauxetic effect.

The ability of common ligands to cause cloud expansion has an order which is similar to spectrochemical series.



fluoride ion < water < ammonia < oxalate < nitrogen < sulphur ion < chloride ion <

Cyanide ion < Bromide ion < Iodine ion.

16/04/2019

HYDROGEN BONDING

Hydrogen bonding is a weak electrostatic attraction between a lone pair of electron on one atom and a covalently bonded hydrogen atom that carries a fractional charge of δ^+ (δ is small)

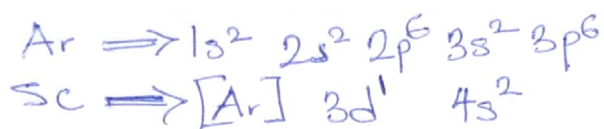
Hydrogen bonds are formed by with the most electronegative atoms such as F, O, N & Cl.

Hydrogen bonds are weak and typically about 10 kJ/mol compared to 347 kJ/mol in covalent bond.

Hydrogen bonds are important in biochemical systems and in normal chemistry, they are important in linking polypeptide chains in proteins and for linking pairs of bases in large nucleic acid containing molecules. A combination of hydrogen bonding with other dipolar forces imposing considerable secondary structure.

Hydrogen bond hold the parallel peptide chain together. Intermolecular hydrogen bond has effect on the physical properties such as melting point, boiling point and the enthalpies of vaporisation and sublimation.

The melting point and the boiling point for a related series of compounds increase as the atoms get larger because of increase in the static dispersive force and also because the additional mass requires higher temperature for a rapid movement of the molecule. By looking at the boiling points of H_2Te , H_2Se & H_2S which are all less than 0°C , it would be expected that the boiling point of H_2O should be about -100°C whilst it is actually $+100^\circ\text{C}$. Thus water boils about 200°C higher than it would in the absence of hydrogen bonding.



THE PERIODIC TABLE

The properties of elements are a periodic function of their atomic numbers - This is called the periodic law. With the help of this periodic law, it is possible to organise a systematic chemistry of the elements into a manageable subject.

Versions of the periodic table

There are 2 versions of the periodic table

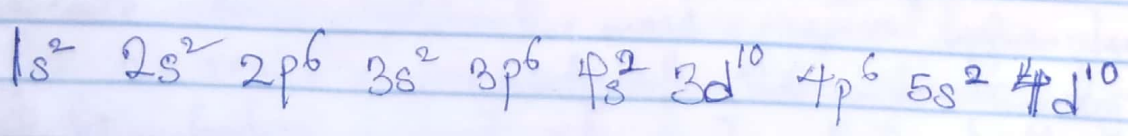
1. A and B subgroups.
2. Long form periodic table.

Since the first publication of the periodic law by Dmitri Mendeleev and Lothar Meyer (1870s), there has been a large number of forms proposed for the periodic table. The only versions easiest to use and most closely related to the electronic structure of the atom is the so called long form shown below

THE PERIODIC TABLE

IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIII 18		
H	He											B	C	N	O	F	Ne		
Li	Be	III B	IV B	V B	VI B					VII B	VIII B	IX B	X B	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	51-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Uup	Lv	Uus	Uuo		

Inner transition elements
 Lanthanide →
 Actinide →

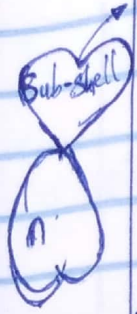


Electronic Configuration

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p

Semi-metals

Boron, ~~Aluminum~~ Silicon, Germanium, Arsenic, Tellurium.
 (B, Si, Ge, As, Te)



The elements fall into 18 vertical columns that define the chemical family, or groups. The members of each group have valence electron configurations that are the same, except for principal quantum numbers. While chemical similarities are most often strongest among elements in the same column, there is some resemblance between elements that are not in the same column but which do have the same number of valence electrons. For example, members of the scandium group have the configuration $(n-1)d^1ns^2$ and, in some respect similar to the element below boron which have the configuration ns^2np^1 . Consequently, the elements under scandium in the 3rd column are said to be members of group IIIA, subgroup B or simply group 3B while the boron family is labelled group 3A. Other groups in the periodic table are related in a similar manner. The elements in the three columns designated group 8B (VIII B) resemble each other in many respects and separate the A subgroup from the B subgroup in the periodic table.

25/07/2019

VARIATIONS OF PHYSICAL PROPERTIES IN THE PERIODIC TABLE

Atomic Radii (Size)

Nuclear charge

Shielding or Screening

Isoelectronic

Ionization energy

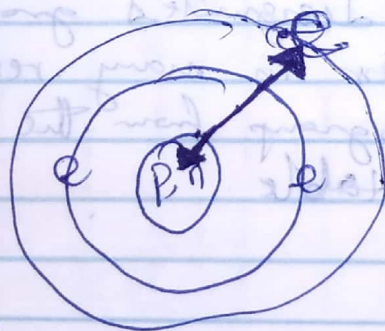
Electron affinity

Electronegativity

Oxides

ATOMIC RADII (SIZE)

Atomic radius is the size of the atom and it is determined by the position of the outermost electron.



Atomic radii decreases across a period from left to right.

The controlling factor here is effective nuclear charge (Z_{eff})

The reason the atomic size decreases across a period is because as the number of electrons increases, the number of protons increases which increases the force of attraction between the proton and electron and causes shrinkage and thus atomic radii decreases.

Down a group, we add additional shell, (principal quantum number) therefore, there is increase in proton and increase in size of atom.

The added shell overpowers the effect of effective nuclear charge Z_{eff} . therefore, down a group. Atomic radii increases

NUCLEAR CHARGE

Across a period, Z_{eff} increases

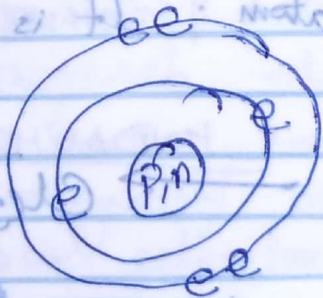
Down a group, Z_{eff} increases

(because both across a period and down a group, proton is being added which causes increase in effective nuclear charge Z_{eff})

SHELDING/SCREENING

Intervening

Intervening electrons shield the outermost ones from the nucleus. Also, two or more electrons on the shell shield each other from the nuclear charge. In any case, shielding weakens the nuclear force on the electrons.



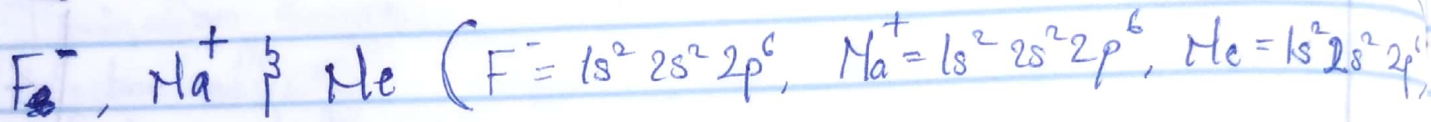
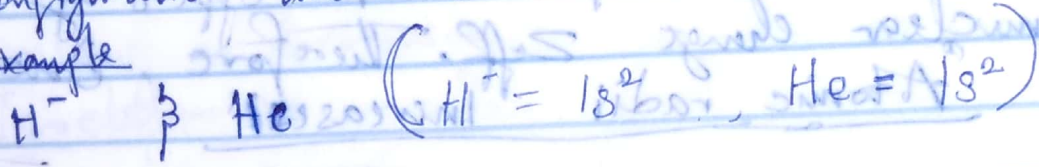
The more electrons we have in the outermost shell, the lesser the nuclear force on the valence electrons.

i.e. $x, x-1, x-2, \dots$

ISOELECTRONIC

Ions (or atoms and ions) that have the same number of electrons, and hence the same electronic configuration are said to be isoelectronic.

Example



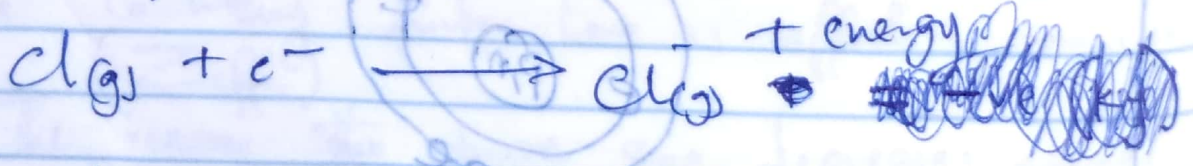
IONIZATION ENERGY

Ionization energy is the amount of energy required to remove completely an electron from the outermost shell of an atom.

Ionization energy decreases down the the group but increases across a period.

ELECTRON AFFINITY

Electron affinity is the energy released or absorbed when an electron is added to a neutral gaseous atom. It is usually an exothermic process.



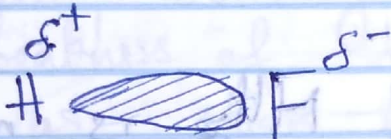
~~Ionization energy increases~~
Electron affinity increases across the period and decreases down a group.

Electronegativity

This is the attraction which an atom has for electrons in a chemical bond

$$\text{Electronegativity} \propto \frac{Z_{\text{eff}}}{\text{valence atomic radius}}$$

Example



Since fluorine is more electronegative, it attracts more electrons to itself.

Electronegativity increases across the period and decreases down the group.

OXIDES

Most metals form alkaline oxide while most non-metal form acidic oxide.

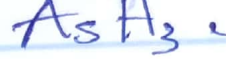
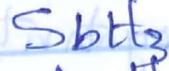
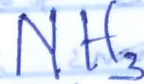
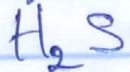
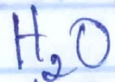
LANTHANIDES & ACTINIDES

LANTHANIDE CONTRACTION

MATERIAL ACQUIRED

Hydrogen Bonding

Continuation



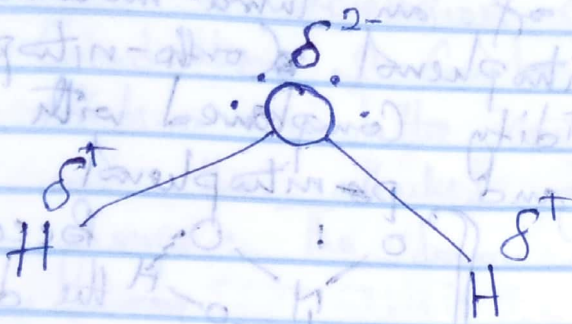
Also the boiling point of NH_3 is much higher than that of PH_3 , SbH_3 & AsH_3 .

Similarly HF boils at higher temperature than HCl , HBr , HI because fluorine takes part in hydrogen bonding.

Water has a much larger effect because each molecule can average 4 hydrogen atoms (2 through the nucleus and 2 through the hydrogen atoms) while HF can only average 2 because it has only one H available.

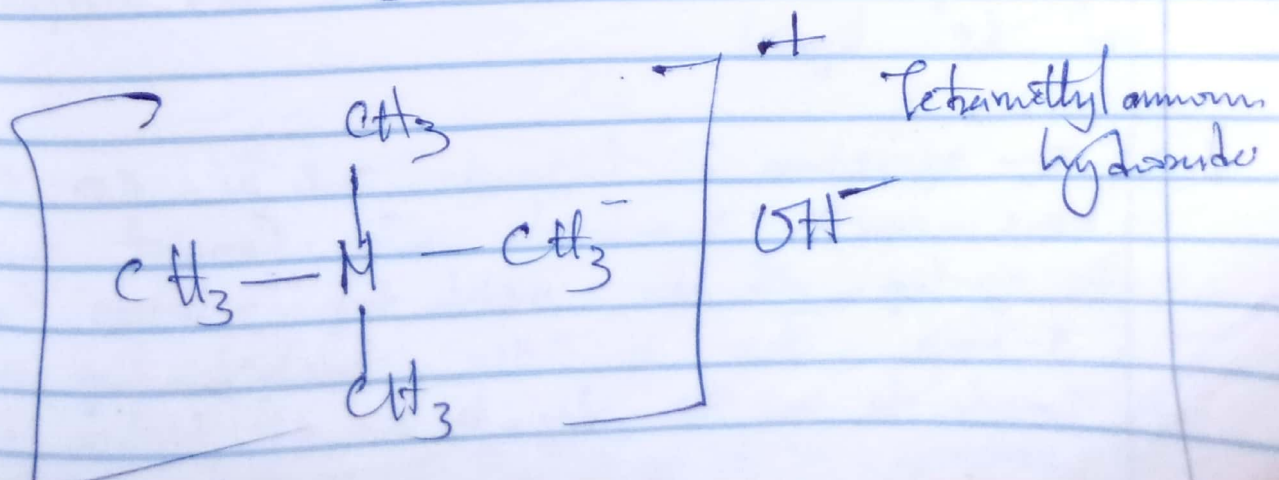
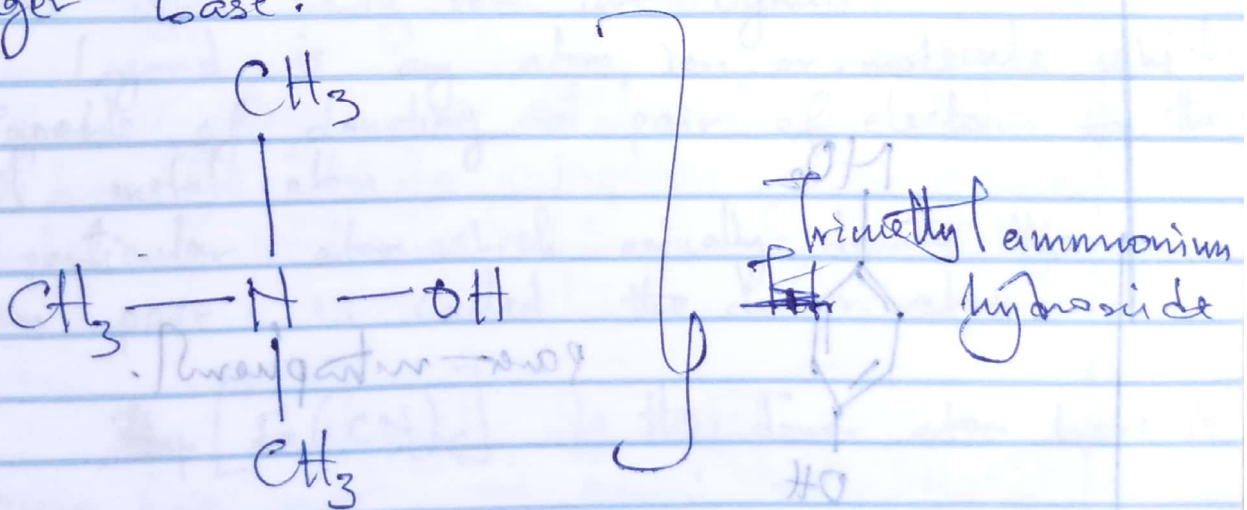
The reason for the higher than expected boiling point is hydrogen bonding.

The freezing point of water is much higher than that of similar molecules, also the density of water decreases as it freezes. Tetrahedral structure around each oxygen with 2 regular bonds to hydrogen and 2 hydrogen bonds to other molecules requires a very open structure with large spaces between the ice molecule. This makes the solid lighter than more random liquid water surrounding it.

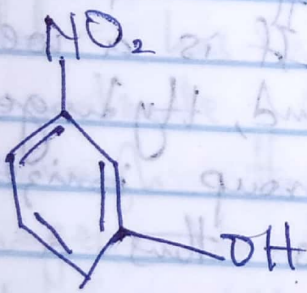
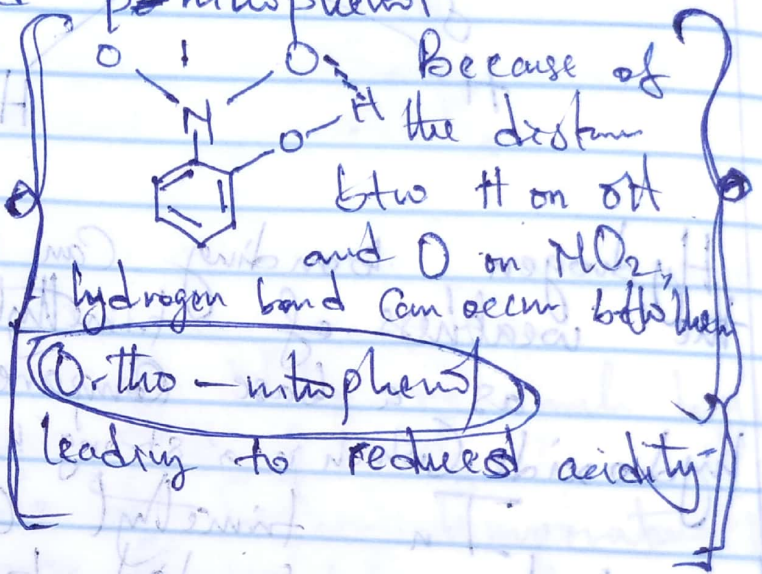
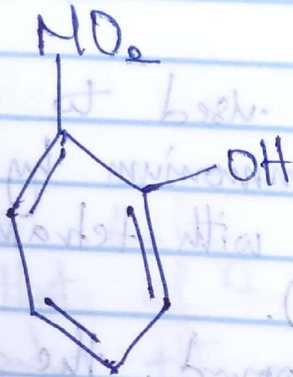


Hydrogen bonding can be used to explain the weakness of trimethyl ammonium hydroxide as a base compared with tetramethyl ammonium hydroxide, (which is a strong base).

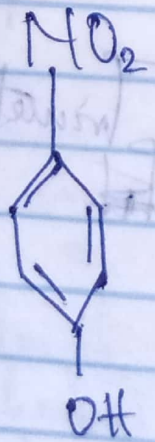
In trimethyl compound, the OH group is hydrogen bonded to the trimethyl ammonium and thus makes it more difficult for the OH group to ionize and hence it is a weak base while in tetramethyl compound, hydrogen bonding cannot occur, so the OH group ionizes and the tetramethyl compound is thus a much stronger base.



* The formation of an intra-molecular hydrogen bond in ortho-nitrophenol (Ortho-nitrophenol) reduces its acidity compared with m-nitrophenol and p-nitrophenol.



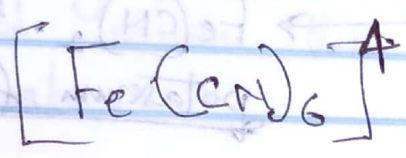
meta-nitrophenol.



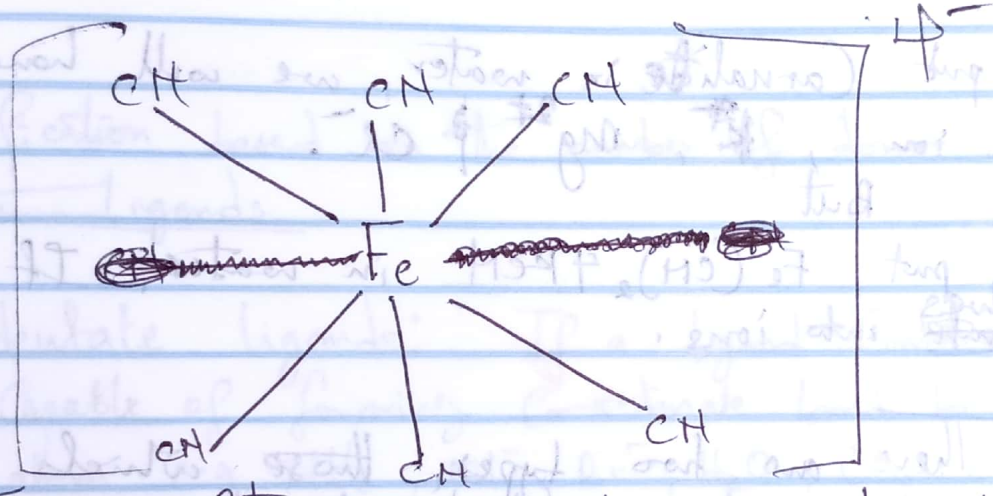
para-nitrophenol.

CO-ORDINATION CHEMISTRY.

Coordination of Complex ~~number~~ ^{Compounds} contains a central atom or ion, the central atom is known as acceptor and the attached groups are known as donor groups. The donor groups are known as ligands. ~~example~~



ferrohexacyanide



The Fe^{2+} ion is the central metal ion or acceptor while CN^- ion are ligand.

Ligand is any atom, ion or molecule which is capable of donating a pair of electrons to the central metal atom.

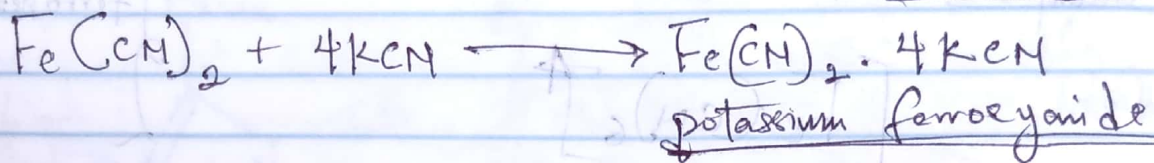
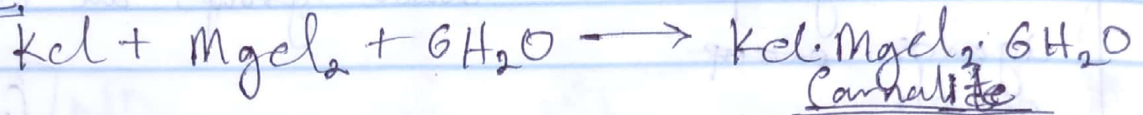
The particular atom which actually donate the electron pair is called the donor atom.

e.g. ~~[Fe(CN)6]~~ $[Fe(CN)_6]^{4-}$, the donor atom here is N

Double salts and Coordination Compounds.

Addition Compounds are formed when stoichiometric amount of two or more stable compounds join together.

Example,



If we put Carnallite in water, we will have 3 different ions K^+ , Mg^{2+} & Cl^- .
But

if we put $Fe(CN)_2 \cdot 4KCN$ in water, it won't ~~disintegrate~~ ^{disintegrate} into ions.

There are two types, those which lose identity in solution; called double salt. and those which retain their identity in solution; called Complexes.

When Carnallite is dissolved in water, the solution shows properties of K^+ , Mg^{2+} and Cl^- but potassium ferrocyanide maintains its identity as a complex.

Types of ligands;
1. Classification based on donor and acceptor properties of the ligand

(a) π -acceptors: ligands such as CO , CN^- & MO^+ have empty π -orbitals with correct symmetry to overlap with the metal t_{2g} orbitals, forming π -bonds. This is called back-bonding and the π -orbitals on the ligands are of higher energy.

than the metal t_{2g} orbitals.

- ⑧ π -donors: The ligands have filled π -orbitals which overlap with the metal t_{2g} orbital, giving a π -bond. This electron density is transferred from the ligand to the metal. The sigma bonding also transfer charge to the metal, this type of complex is favoured when the central metal has a high oxidation state.

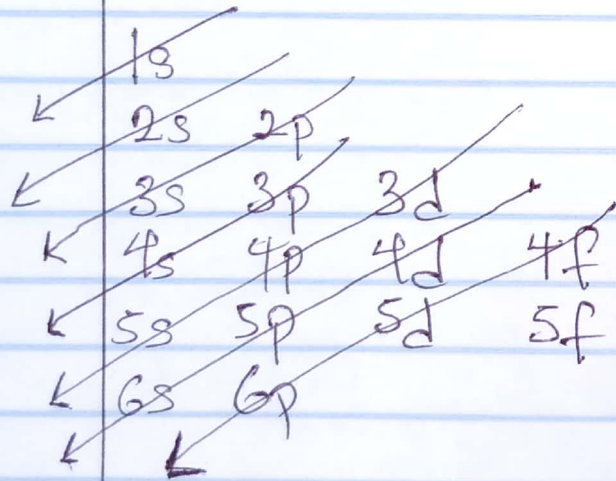
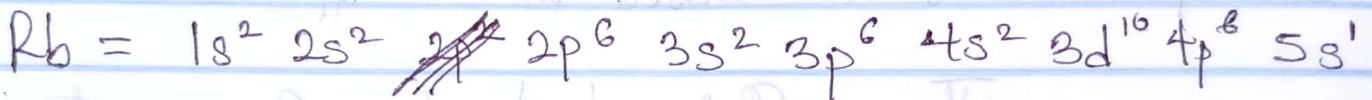
Classification based on the number of donor atoms present in the ligands

1. Monodentate ligands: If a ligand contains only one atom capable of forming coordinate bond to the central metal atom e.g. NH_3 , OH^- , Br^- , H_2O , CO_2 , CS , NO .
2. Polydentate ligands: This is when a ligand has two or more donor atoms which may simultaneously coordinate to a metal atom. The ligand may be bidentate, two donor atoms of acetyl acetone, 2,2'-dipyridyl oxalate, dimethylglyoxime.
3. Tridentate ligands: are diethylenetriamine and imino diacetone acid anion.

Rb =

Ionization energy

Atomic no	Symbol	I_1	I_2	I_3	I_4
37	Rb	403.0	2632.6	3827.0	5080.0



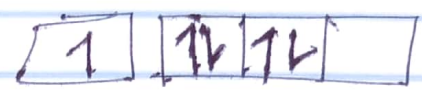
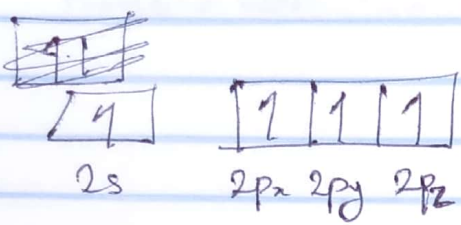
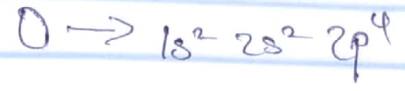
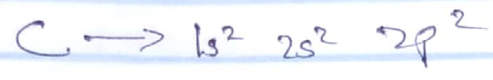
Prof Okolo

TRENDS IN THE CHEMICAL PROPERTIES OF THE PERIODIC TABLE

- Q₁ Why do the chemistry of group IA essentially that of their M^+ ions.
- Q₂ Discuss the ionic & covalent behaviours in group IA elements.
- Q₃ Why is the chemistry of lithium strange in the group IA elements?

Valence bond Theory

1. CO₂

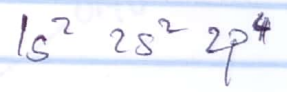
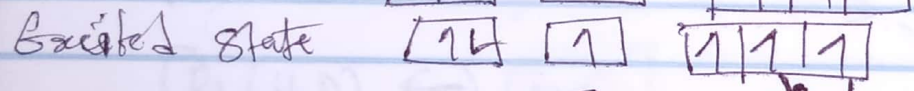
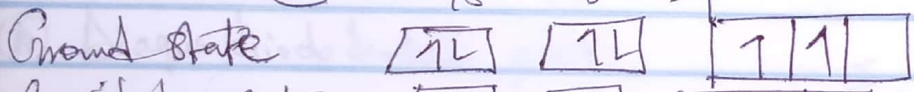
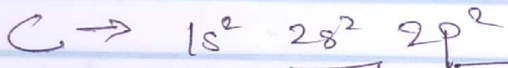


2. Using V.T.B, explain C₂F₈H

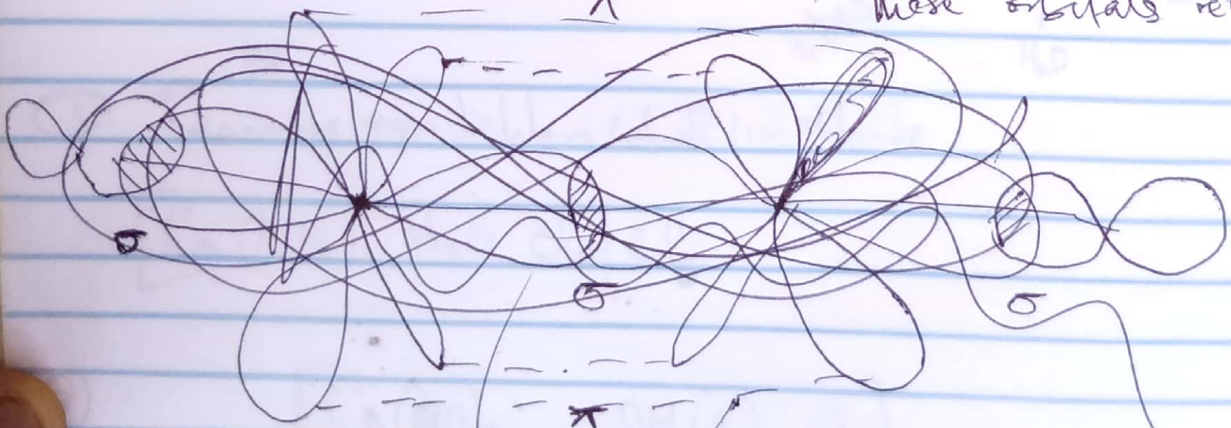


Solution

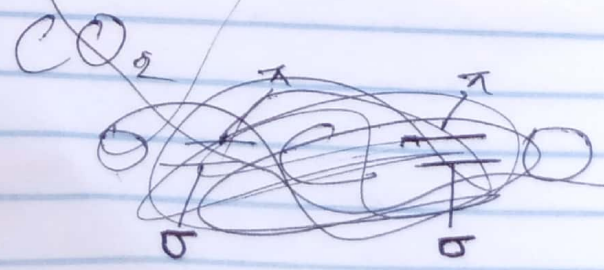
1. CO₂

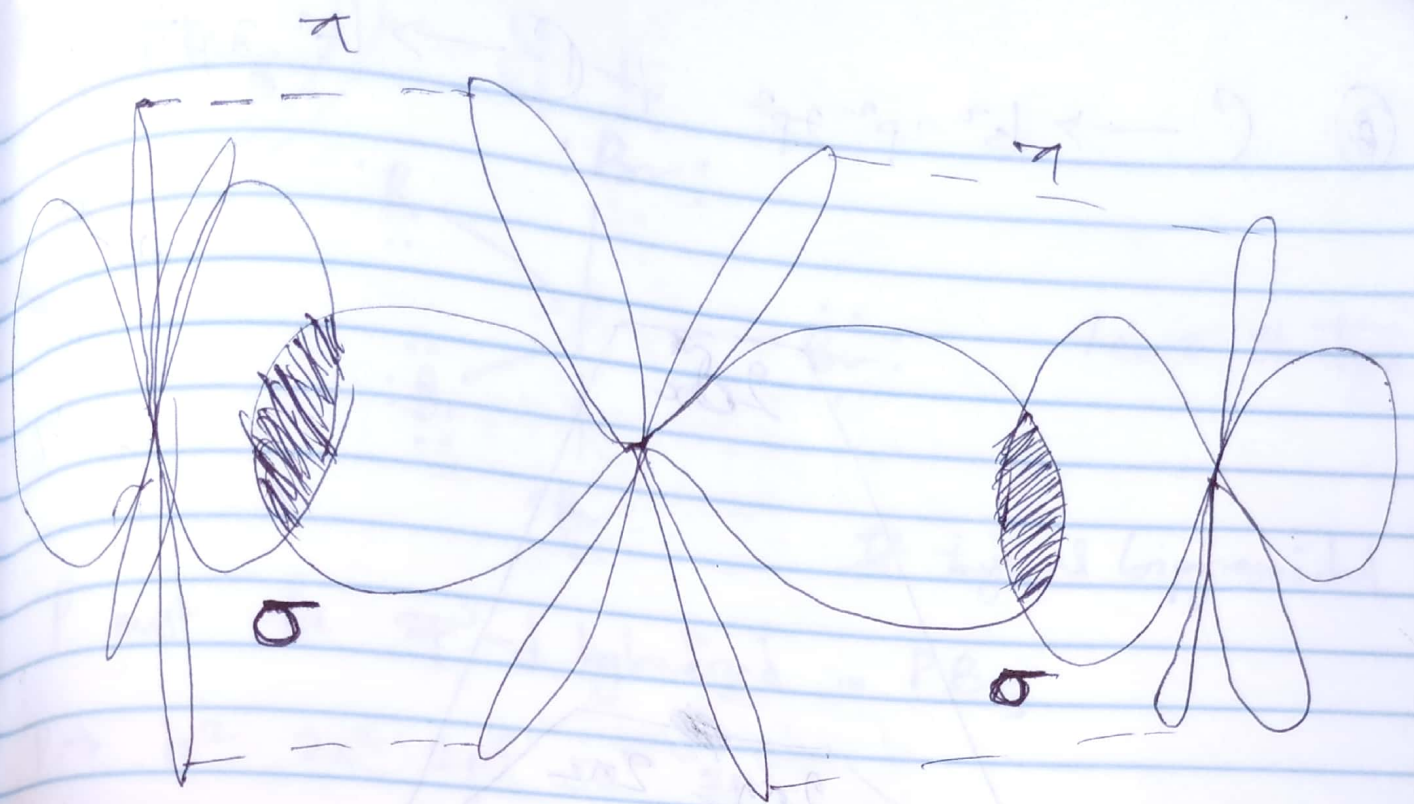


s p sp
These orbitals remain unchanged

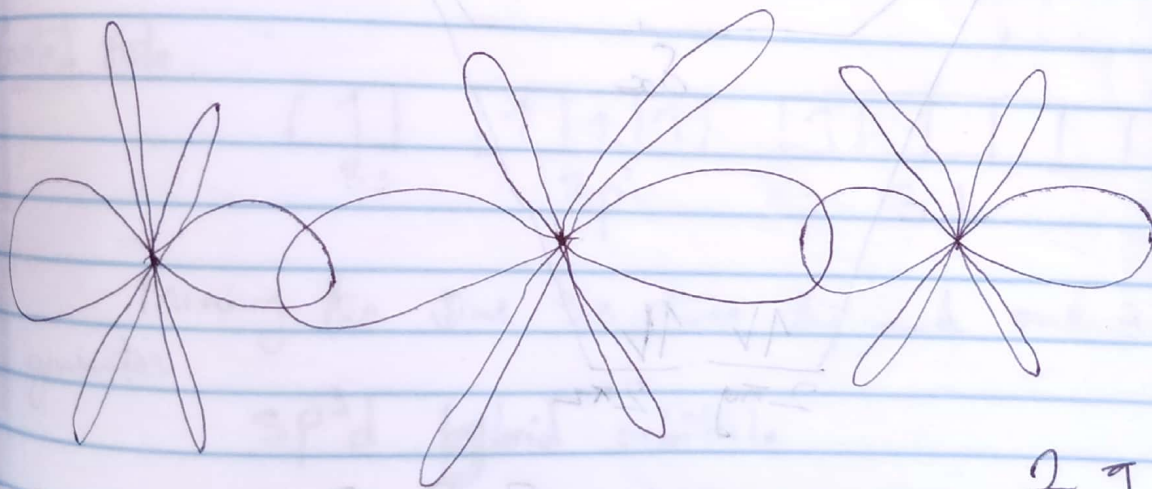


3 σ bond
2 π bond

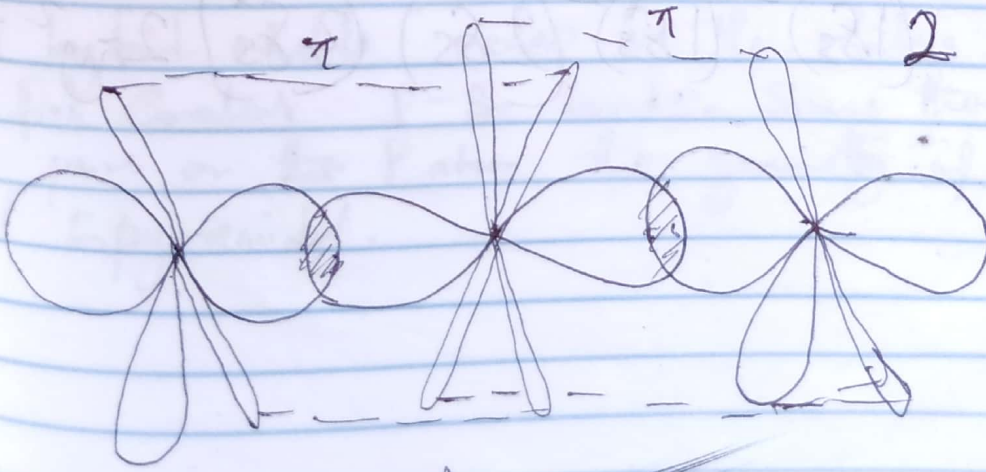


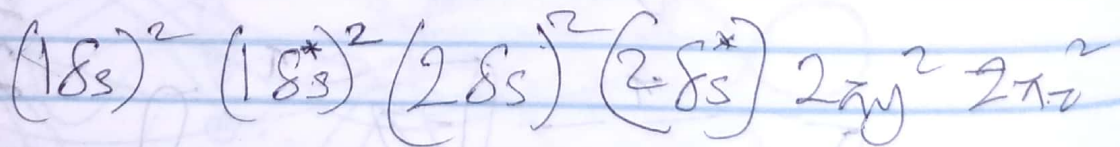
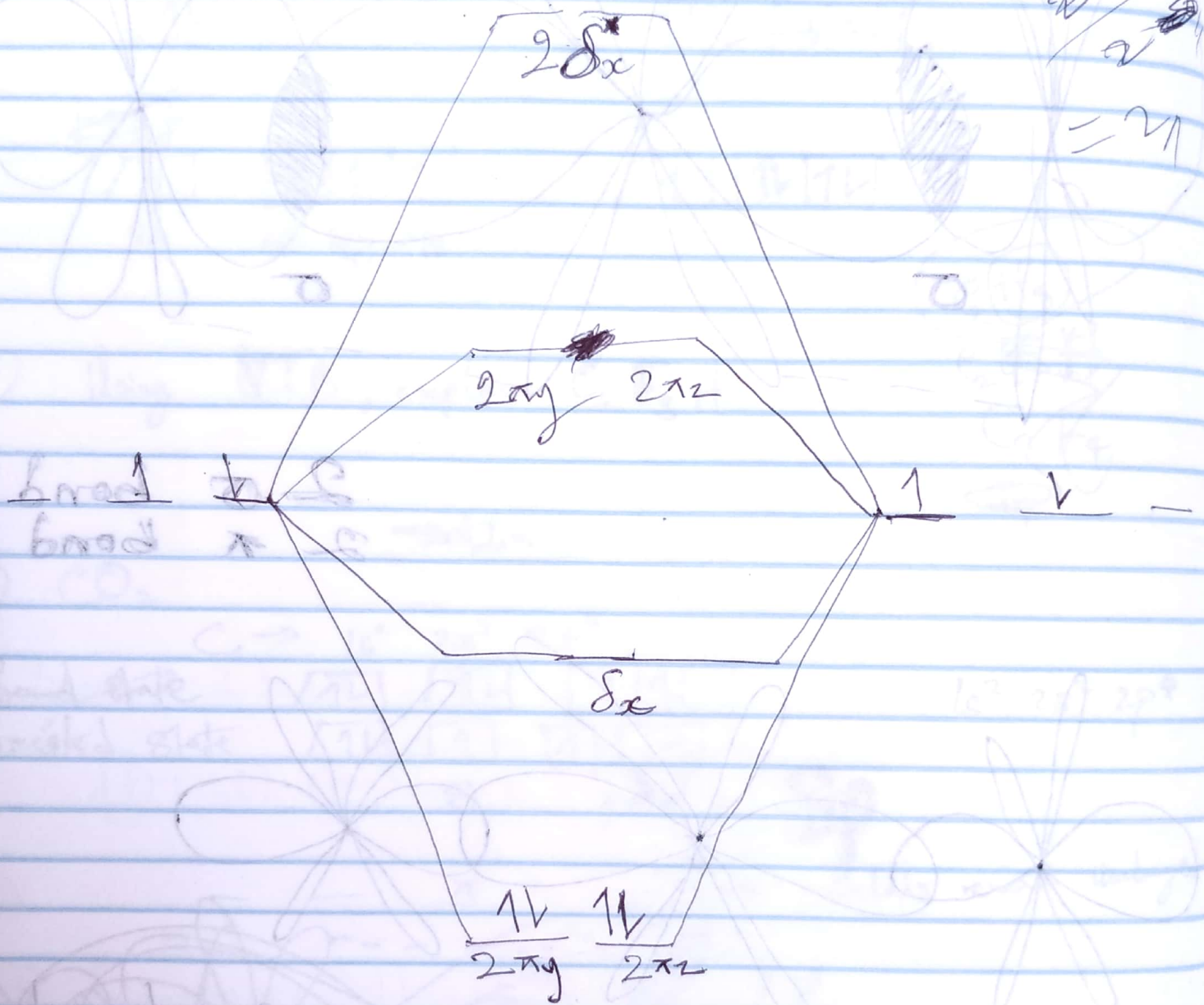
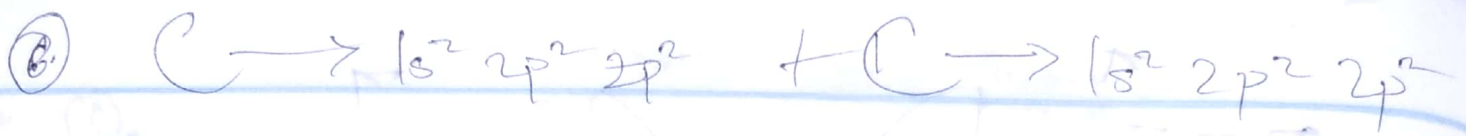


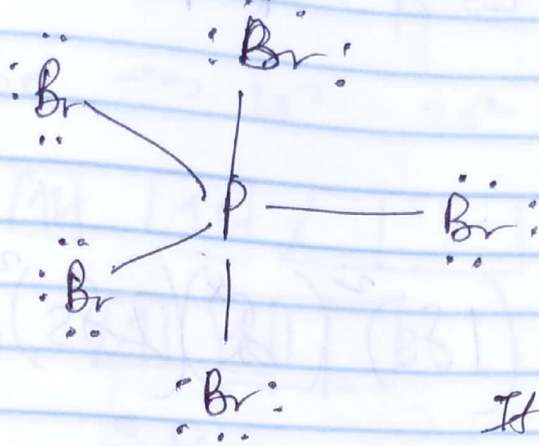
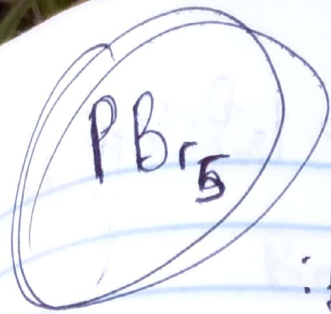
2 σ bond
2 π bond



2 π bond
2 σ bond



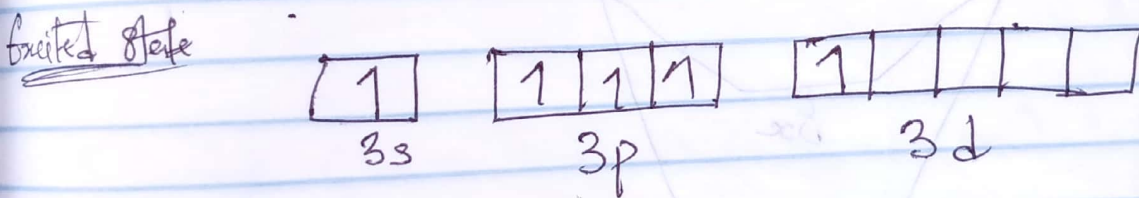
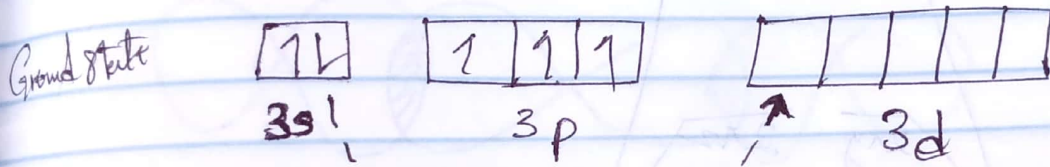
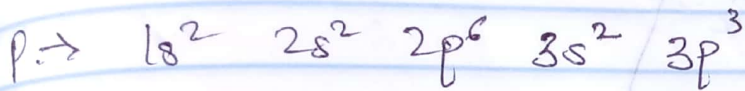




Lewis structure

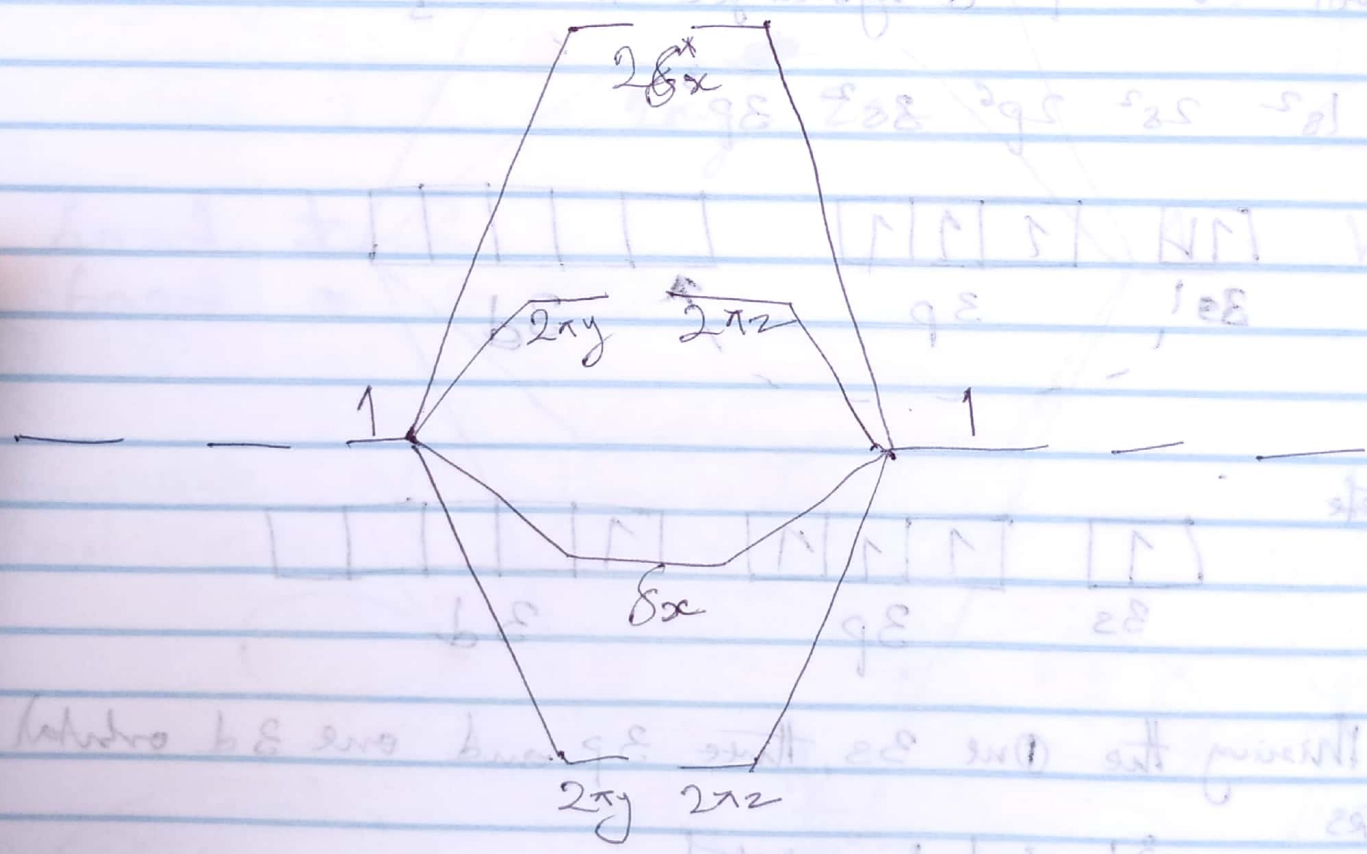
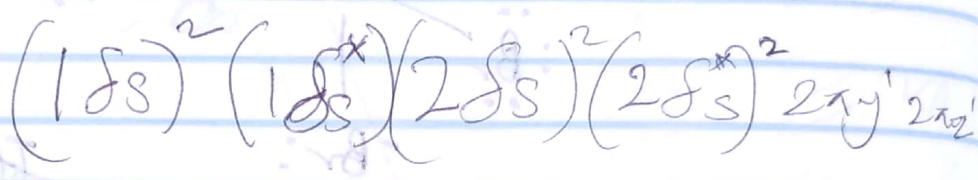
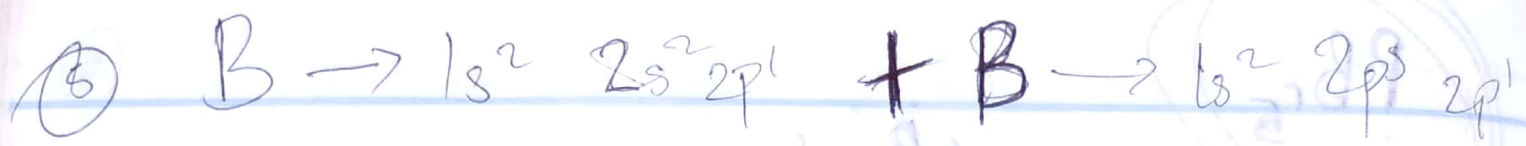
It is trigonal bipyramidal

P must be sp^3d hybridized in PBr_5

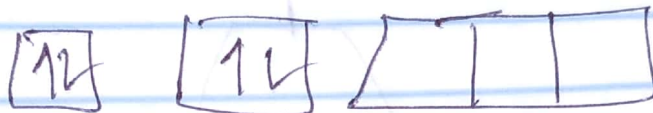
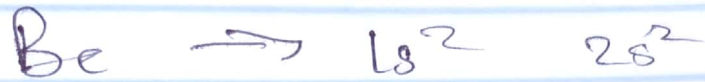


Mixing the one 3s, three 3p, and one 3d orbital generates sp^3d hybrid orbital.

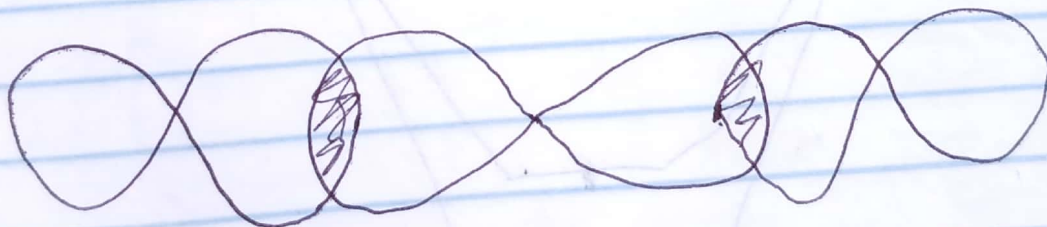
These hybrid orbitals overlap the 4p orbitals of Br to form five covalent P-Br bonds. Since there is no lone pair on the P atom, the geometry of PBr_5 is trigonal bipyramidal.

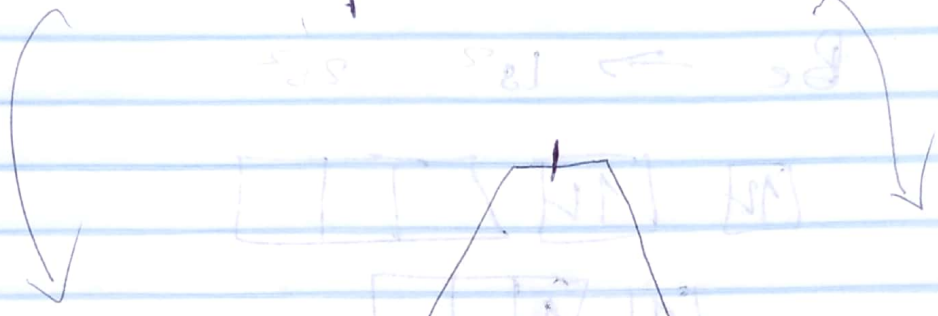


BeCl₂



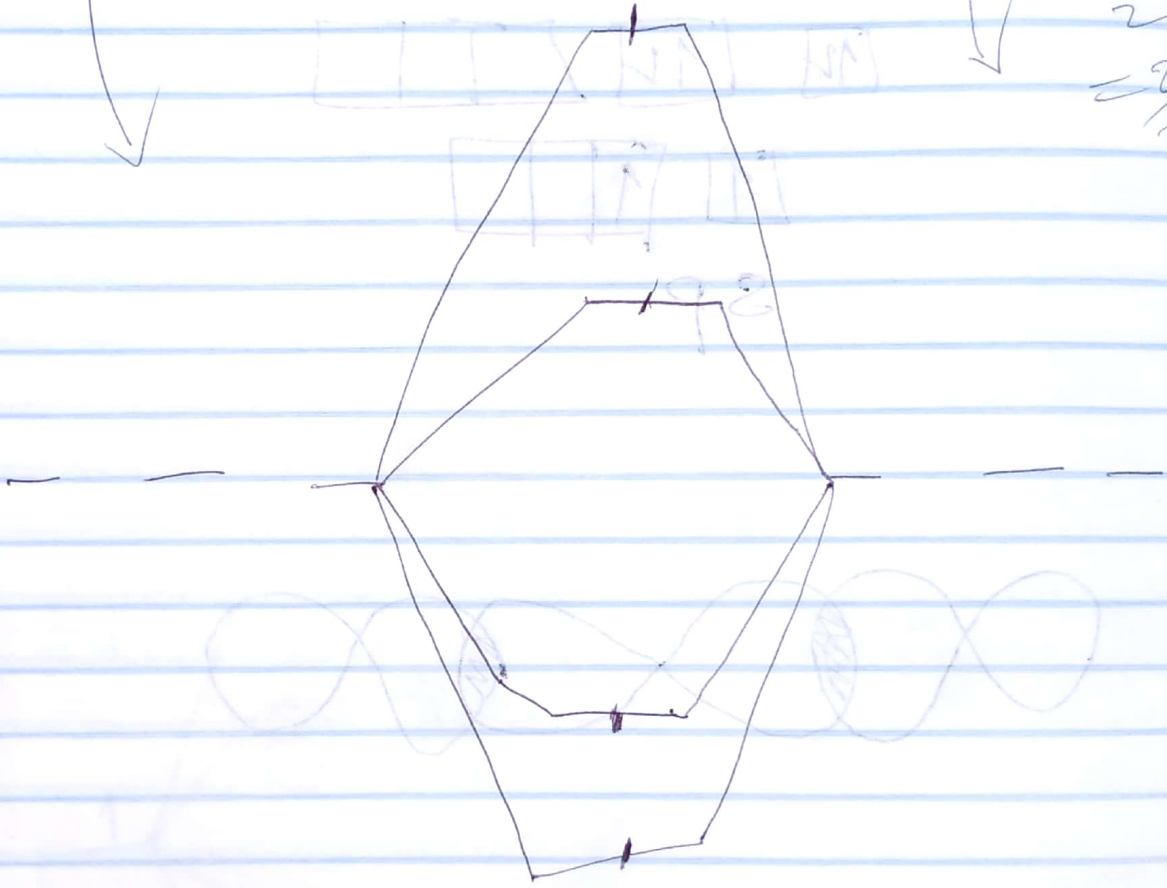
sp



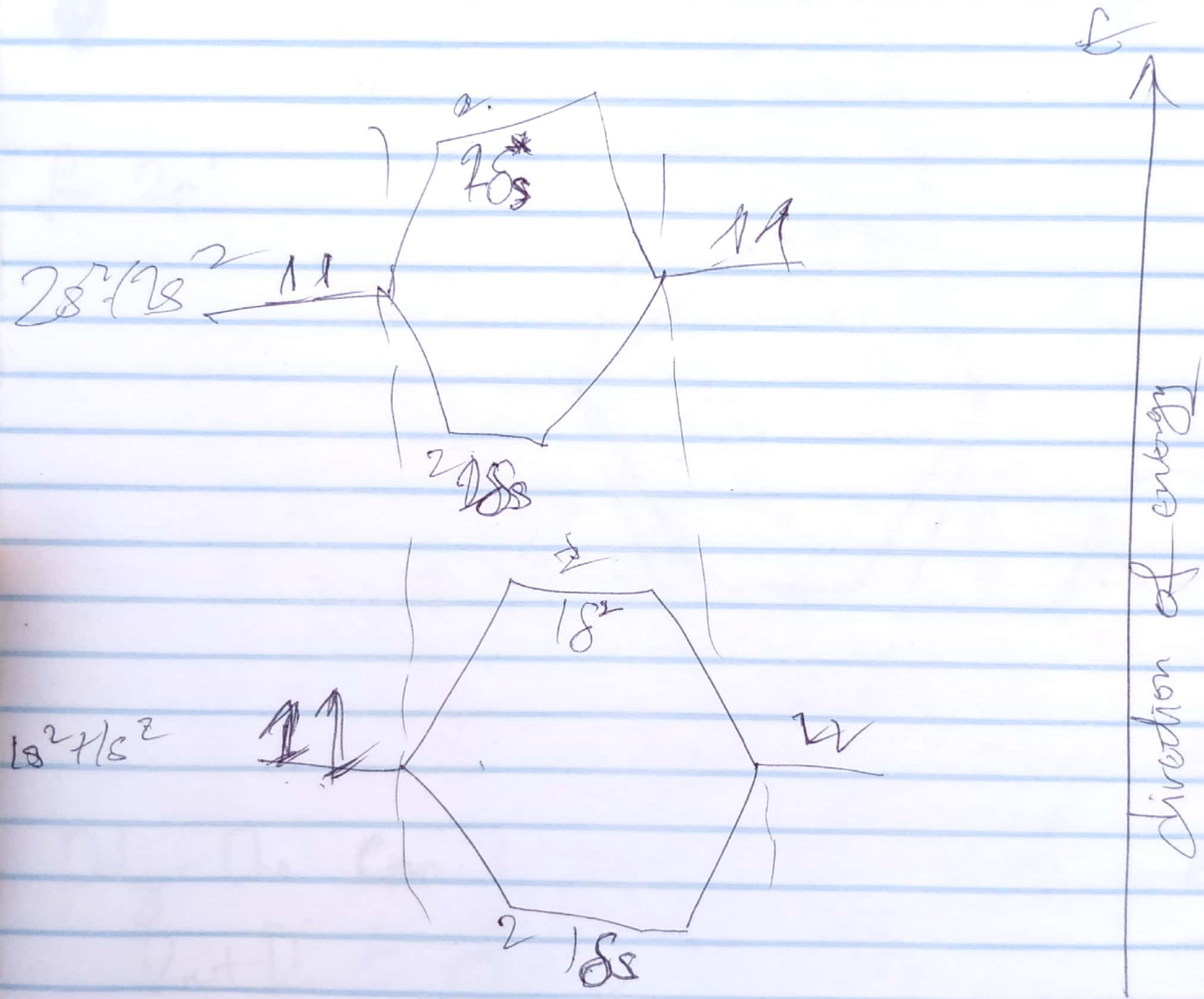
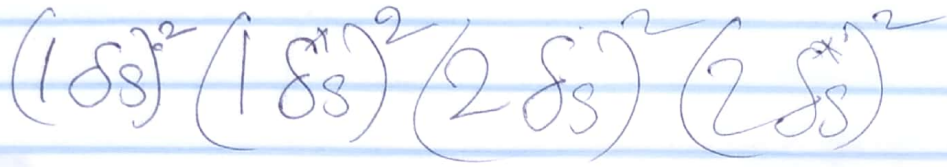


$$\begin{array}{r}
 6 - 4 \\
 \hline
 2 \\
 = 2 \\
 \hline
 2
 \end{array}$$

for $2p^1$



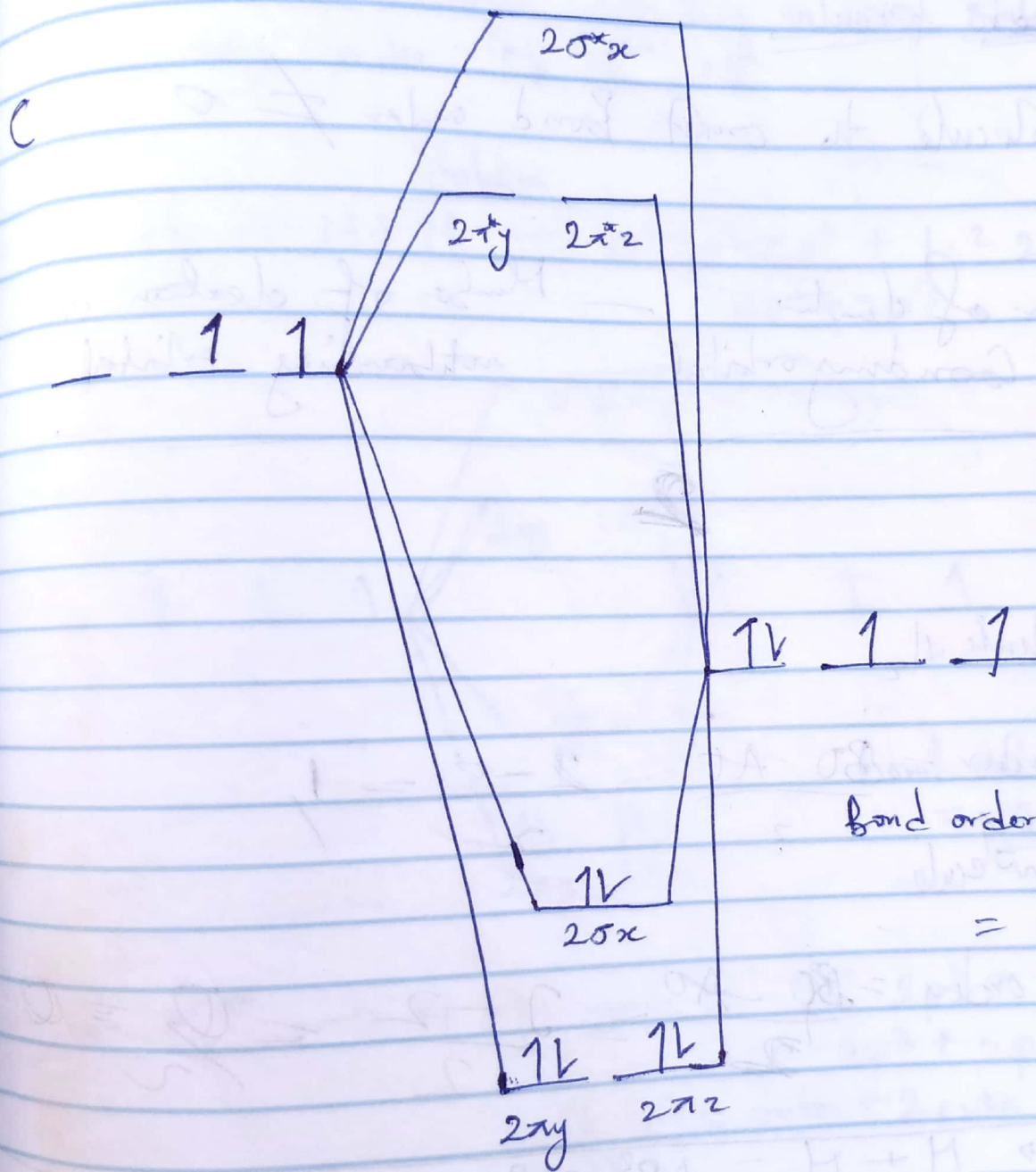
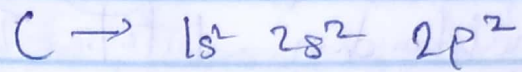
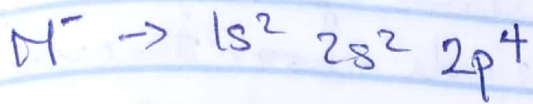
Only one can be used to form a σ bond
 $2p_x + 2p_x = \sigma_x$



$$\text{Bond order} = \frac{4 - 0}{2} = \frac{4}{2} = 2$$

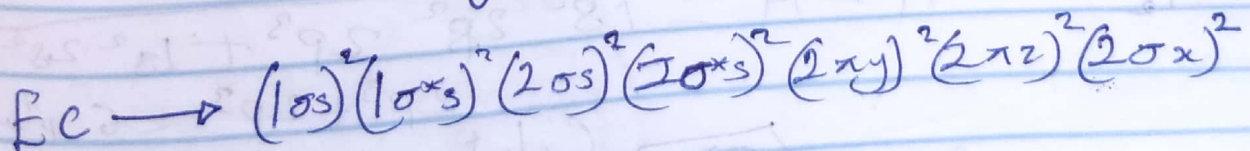
In octahedral, the e_g set of orbitals (d_{z^2} & $d_{x^2-y^2}$) have the higher energy, while in square planar, the $d_{x^2-y^2}$ orbital possesses the highest energy (just like in octahedral case) and the d_{xy} orbital has the next highest. However, the relative placement of the d_{z^2} and the d_{xz} and d_{yz} orbitals cannot be determined simply by inspection & must be calculated.

CN⁻



$$\text{Bond order} = \frac{B.O. - A.O.}{2}$$

$$= \frac{8 - 0}{2} = \underline{\underline{4}}$$



② He $\rightarrow 1s^2$ (This molecule does not exist)
Note for a molecule with equal number of electrons in bonding and antibonding orbitals. The molecule won't exist.
Bond order formula.

For a molecule to exist Bond order $\neq 0$

$$\frac{\text{Number of electrons in bonding orbital}}{\text{Number of electrons in antibonding orbital}}$$

2

for Hydrogen molecule H_2 $\uparrow \uparrow$

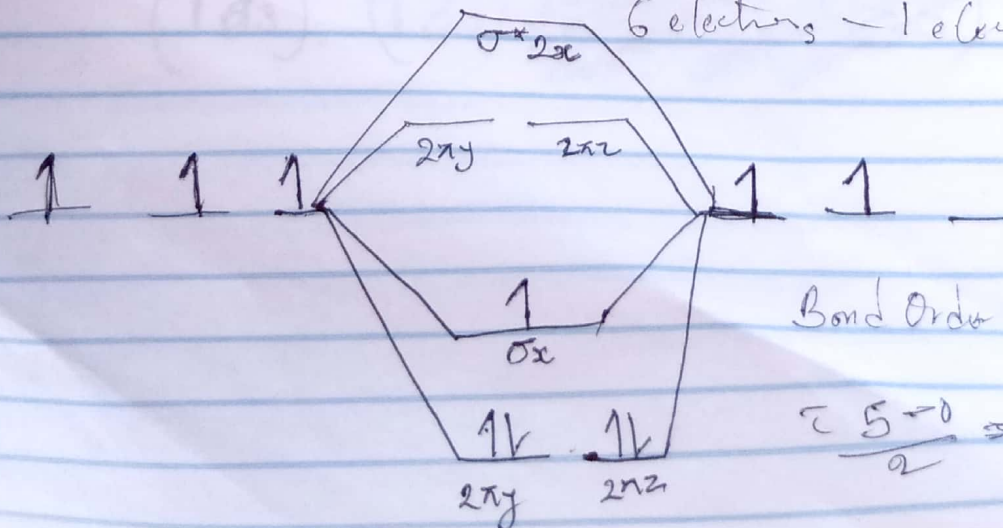
$$\text{Bond order} = \frac{BO - AO}{2} = \frac{2 - 0}{2} = 1$$

for Helium molecule

$$\text{Bond order} = \frac{BO - AO}{2} = \frac{2 - 2}{2} = 0 \equiv 0$$

For $N_2^+ \rightarrow N + N = 1s^2 2s^2 2p^3 + 1s^2 2s^2 2p^3$

6 electrons - 1 electron = 5 electrons

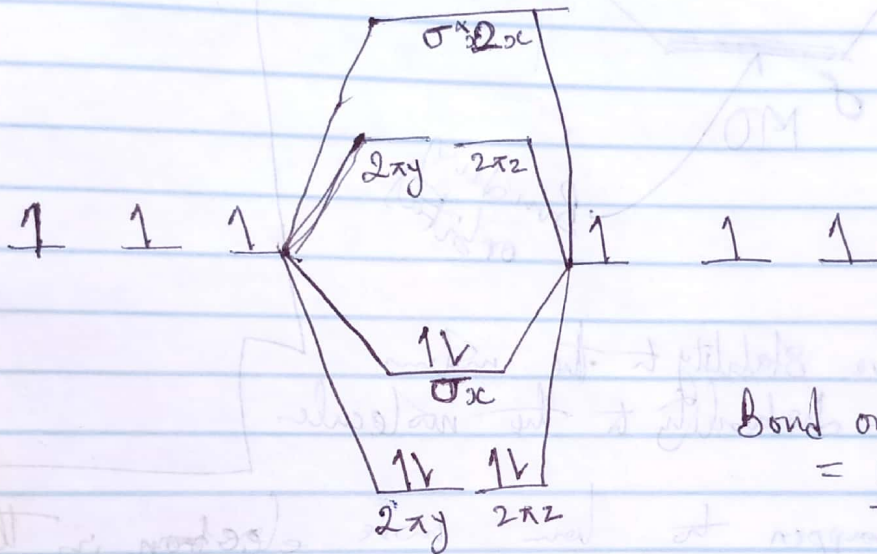
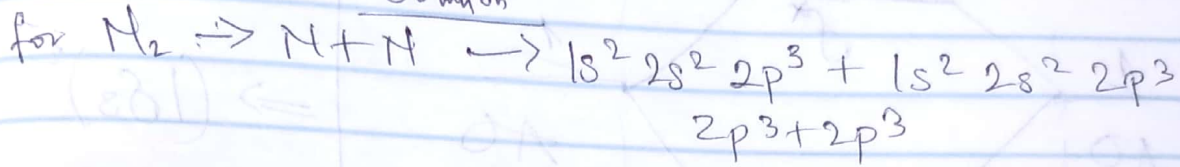


$$\text{Bond Order} = \frac{BO - AO}{2} = \frac{5 - 0}{2} = 2.5$$

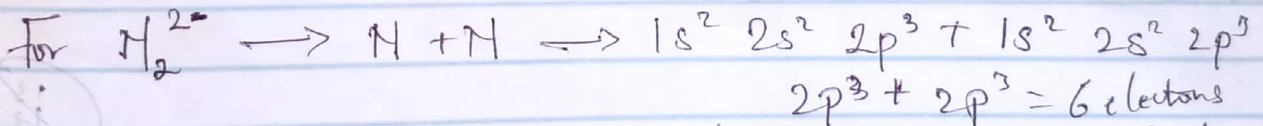
Question

Draw the molecular orbital energy level diagram, Calculate the bond order and arrange the following hypothetical molecules of Nitrogen according to their stabilities in increasing order: N_2 , N_2^{2-} , N_2^+ .

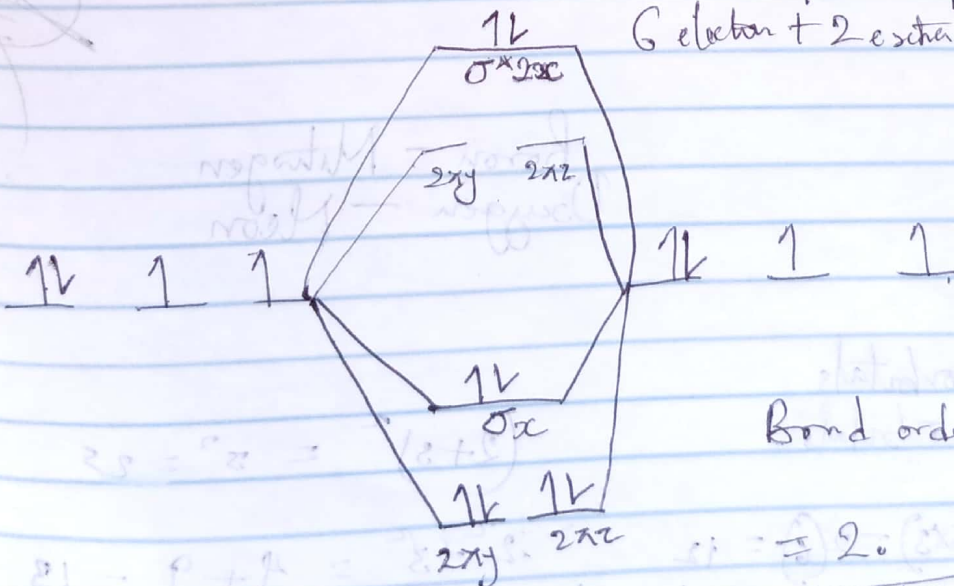
Solution



Bond order
 $= \frac{10 - 4}{2} = \frac{6}{2} = 3$



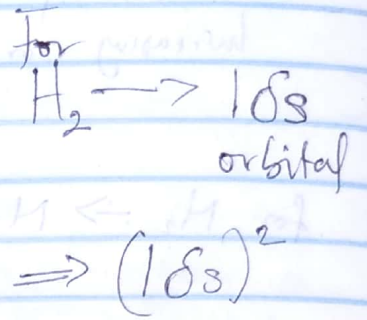
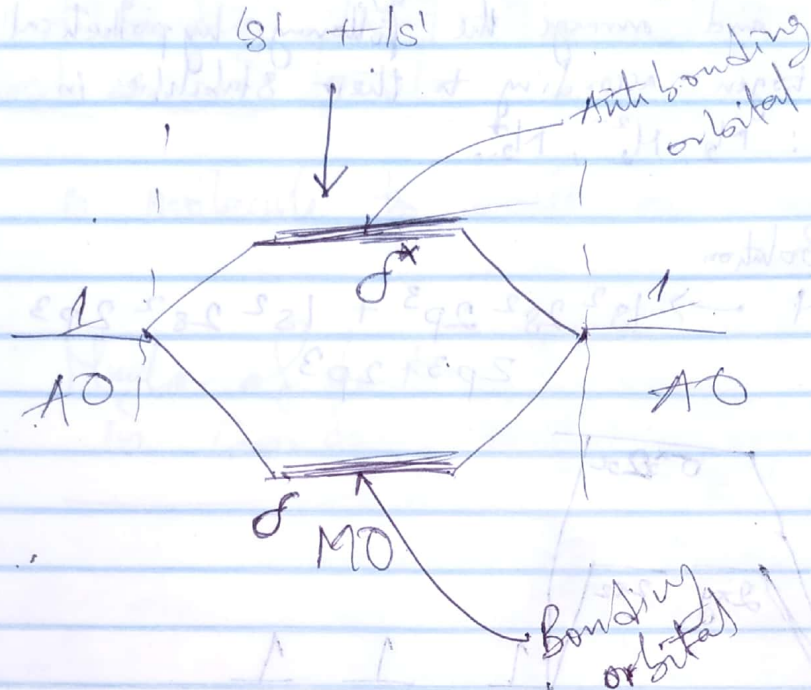
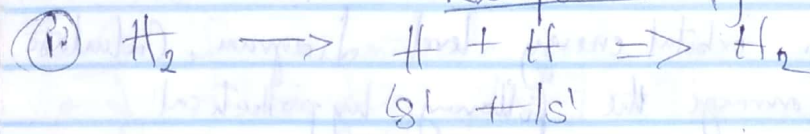
6 electron + 2 extra ones = 8 electrons



Bond order = $\frac{10 - 6}{2} = \frac{4}{2} = 2$

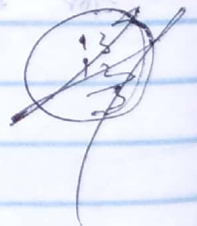
Conclusion Bond order for N_2 , N_2^{2-} and N_2^+ are 3, 2 & 2.5 respectively and Bond order \propto stability therefore, arranged with increasing stability. $N_2^{2-} \Rightarrow N_2 \Rightarrow N_2^+$

Examples of molecular orbitals



Bonding orbital - Give stability to the molecule
 Antibonding orbital - Disturbance to the molecule

It can never happen to have more electron in the ABO than the BO



Boron - Nitrogen
 Oxygen - Neon

Atomic orbitals
 Molecular orbitals

$$(2+3)^2 = 5^2 = 25$$

$$2(2 \times 3) = 2(6) = 12$$

$$2^2 + 3^2 = 4 + 9 = 13$$

$$(2+3)^2 > 2^2 + 3^2$$

and the difference is $2(2 \times 3)$

CHAPTER TWELVE

COORDINATE CHEMISTRY

12.1. Definition of Terms

A. Ligands

Ligands are anions or neutral molecules that are bind to metal atom/ion through coordinate covalent bonds to form complexes. They are Lewis bases because they are electron-pair donors.

Denticity of a ligand is the number of coordinate covalent bond (s) or donor groups in a single ligand that bind to a central metal atom/ion in a complex or ion.

Ligands can be classify into three based on their coordination number (dentation).

1. **Monodentate Ligands**: These are ligands that have only one donor atom and are coordinated to metal ion through single covalent bond (through one pair of electrons) e.g Cl^- , NH_3 , CN^- e.t.c.
2. **Bidentate Ligands**: These are ligands with two donor atoms and are coordinated to metal ion through two covalent bonds (through two electron pairs) e.g $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, NH_2NH_2 , $\text{C}_2\text{O}_4^{2-}$ e.t.c.
3. **Polydentate/Chelating Ligands**: These are ligands that are bonded to metal ions through more than two atoms. They are also known as *chelating agent* e.g ethylene diamine tetraacetic acid (EDTA) is tetradentate,

Table 12.2: Examples of neutral ligands and their dentations

Ligands	Name	Name as ligands
1. CO	Carbon monoxide	Carbonyl (monodentate)
2. H ₂ O	Water	Aqua/ aquo (monodentate)
3. NH ₃	Ammonia	Ammine (monodentate)
4. NH ₂ - NH ₂	Hydrazine	Diamine (bidentate)
5. NH ₂ CH ₂ CH ₂ NH ₂	Ethane diamine	Ethylene diamine

B. Complex ion

A complex ion is a metal atom or ion with Lewis bases or ligands attached to it through coordinate covalent bonds. E.g [Fe(NH₃)₆]²⁺ is a cationic complex ion while [Ni(CN)₄]²⁻ is an anionic complex ion.

C. Complexes/ Coordination Compounds

A complex is a compound consisting of a complex ion and ion of opposite charge e.g The complex K₂[Ni(CN)₄] consist of complex ion [Ni(CN)₄]²⁻ and K⁺ ions.

D. Coordination Number

A coordination number is the total number of coordinate covalent bonds the ligands form with the central metal atom/ion in a complex/ complex ion. In other words, it is the number of donor atoms bonded to the central metal atom/ion. It is given by the formula:

$$C.N = \text{Number of ligands} \times \text{dentation}$$

e.g What is the coordination number of [Pt(NH₃)₄(Cl₂)]?

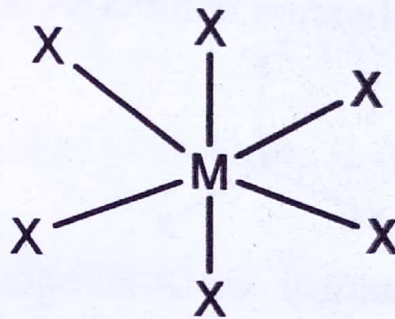
Solution: Dentation of ammine is 1; number of ammine is 4
 Dentation of chloro is 1; number of chloro is 2

But:

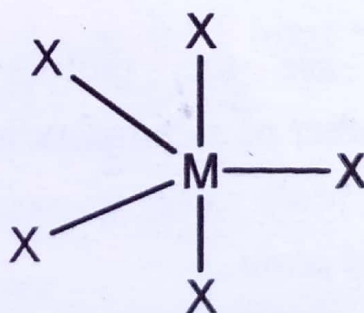
$$C.N = \text{Number of ligands} \times \text{dentation} = (4 \times 1) + (2 \times 1) = 6$$

Remember: Using valence bond theory, a;

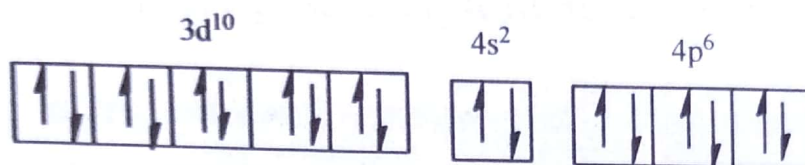
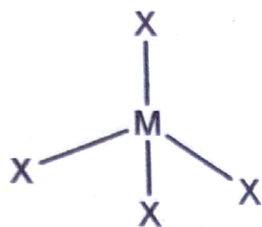
- a. Coordination number of 6 is equivalent to octahedral shape with sp^3d^2 hybridization and bond angle of 90° .



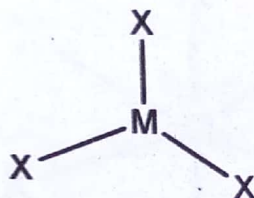
- b. Coordination number of 5 is equivalent to trigonal bipyramidal and square bipyramidal shapes with sp^3d hybridization and bond angles of 90 and 120° .



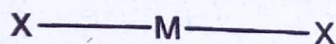
- c. Coordination number of 4 is equivalent to square planer with sp^2d hybridization (as in a strong field ligand with bond angle of 120° (e.g $[\text{Ni}(\text{CN})_4]^{2-}$) or tetrahedral with sp^3 hybridization and bond angle of 90° in a weak field ligand (e.g $[\text{Ni}(\text{H}_2\text{O})_4]^{2-}$).



- d. Coordination number of 3 is equivalent to trigonal planar shape using sp^2 or sd^2 configuration with bond angle of 120° . The coordination number of 3 is rare.



- e. coordination number of 2 is equivalent to linear shape mostly for Cu, Ag, Au and Hg complex ions with d^{10} configuration as in $[\text{NH}_3\text{-M-NH}_3]^+$. The hybridization of the central metal is sp and bond angle of 180° .



The following are the factors that determine the coordination number of a complex/ion:

- *Size of the central atom*
- *Number of d-orbital electrons*
- *Steric effect arising from the ligands*

E. Principal Oxidation Number (P.O.N.)

This is the oxidation state of the central metal ion in a complex or complex ion. For instance, determine the number oxidation state of platinum in $[\text{Pt}(\text{NH}_3)_4(\text{Cl}_2)]^{2+}$.

Solution: The complex ion $[\text{Pt}(\text{NH}_3)_4(\text{Cl}_2)]^{2+}$ has two kinds of ligands around the central atom: Four NH_3 and two Cl^- . The charge on the ammine ligands is zero (neutral ligands), the charge on each Cl^- is -1, and the overall charge is +2. Denoting the charge on Pt ion as x, we have:

$$x + 4(0) + 2(-1) = +2 ; \quad x + 0 - 2 = +2; \quad x = +4$$

Thus, the oxidation number of platinum in the complex is +4.

F. Effective Atomic Number (EAN)

Effective Atomic Number (EAN) is the total number of electrons surrounding the nucleus of a metal atom in a metal complex or complex ion. It is composed of the metal atom's electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. Thus:

$$\text{EAN} = Z - \text{charge on the metal} + \text{total electrons supplied by ligands}$$

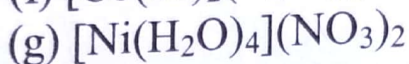
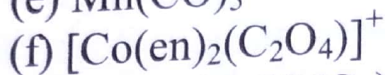
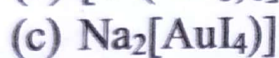
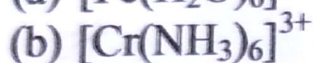
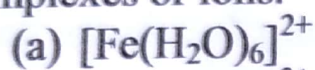
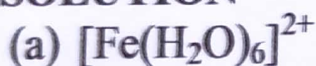
Note: *Number of electrons from each ligand = 2 x dentation*

The *EAN rule* states that, in a number of metal complexes, the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble-gas element found in the same period in which the metal is situated. In other words, a complex is said to

be stable if the total d-orbital electrons from the transition metal, the total electrons supplied by the ligands and the overall charge of the complex equals 18.

EXAMPLE 12.1

Determine the principal oxidation number, coordination number, hybridization of central metal, bond angle, geometry, effective atomic number and the stability of each of the following complexes or ions:

**SOLUTION**(i) Let the oxidation number of iron be F ;

$$F + 6(0) = +2 \quad (\text{H}_2\text{O} \text{ is a neutral ligand})$$

$$F = +2$$

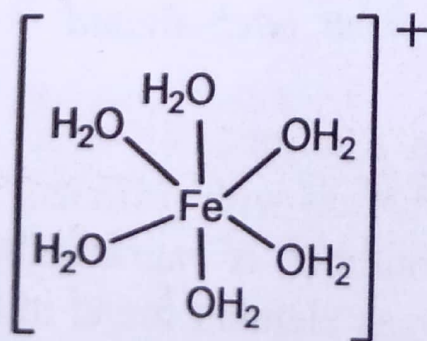
Therefore, the principal oxidation number of Fe is +2

(ii) Coordination number, C.N = Number of ligand + dentation
 $= 6 \times 1 = 6$

(iii) sp^3d^2 hybridization

(iv) Bond angle of 90°

(v) The geometry is octahedral



$$(vi) \quad E.A.N = 26 - 2 + (2 \times 6) = 26 - 2 + 12 = 36$$

- (vii) The electron configuration of Fe^{2+} is $[Ar] 3d^6$
 Number of electrons from d - subshell = 6
 Number of electrons from ligands = $2 \times 6 = 12$
 Total electrons = $6 + 12 = 18$

The complex ion is stable according to E.A.N. rule since the total electrons is equal to 18



- (i) Let the oxidation number of chromium be C ;

$$C + 6(0) = +3 \quad (NH_3 \text{ is a neutral ligand})$$

$$C = +3$$

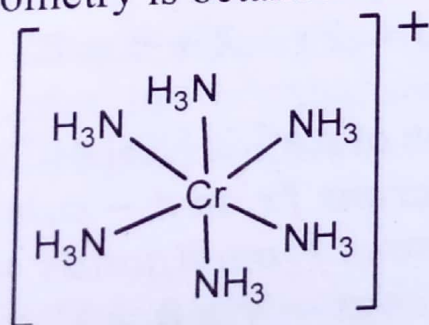
Hence, the principal oxidation number of Cr is +3

- (ii) Coordination number = $6 \times 1 = 6$

- (iii) sp^3d^2 hybridization

- (iv) Bond angle of 90°

- (v) The geometry is octahedral



$$(vi) \quad E.A.N = 24 - 3 + (2 \times 6) = 24 - 3 + 12 = 33$$

- (vii) The electron configuration of Cr^{3+} is $[Ar] 3d^3$
 Number of electrons from d - subshell = 3
 Number of electrons from ligands = $2 \times 6 = 12$
 Total electrons = $3 + 12 = 15$

The complex ion is unstable according to E.A.N. rule since the total electrons is less than 18

(c) $\text{Na}_2[\text{AuI}_4]$

(i) Let the oxidation number of gold be G ;

$$G + 4(-1) + 2(+1) = 0 \quad (\text{O.N of iodide ion is } -1)$$

$$G = +2$$

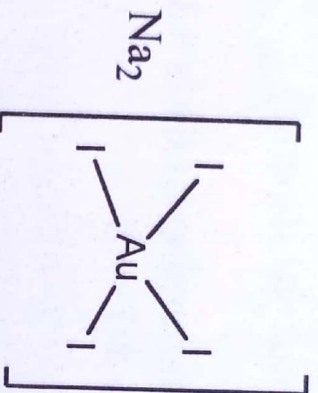
Hence, the principal oxidation number of Au is +2

(ii) Coordination number = $4 \times 1 = 4$

(iii) sp^2d hybridization

(iv) Bond angle of 120°

(v) The geometry is square planer



(vi) $E.A.N = 79 - 2 + (2 \times 4) = 79 - 2 + 8 = 85$

(vii) The electron configuration of Au^{2+} is $[\text{Xe}] 4f^{14}5d^9$

Number of electrons from d - subshell = 9

Number of electrons from ligands = $2 \times 4 = 8$

Total electrons = $9 + 8 = 17$

The complex ion is unstable according to E.A.N. rule since the total electrons is less than 18

(d) $[\text{Pt}(\text{NH}_3)_2\text{Br}_4]$

(i) Let the oxidation number of platinum be P ;

$$P + 2(0) + 4(-1) = 0$$

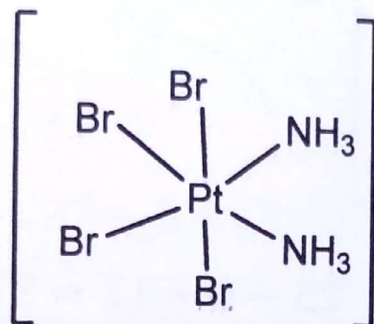
$$P + 0 - 4 = 0$$

$$P = +4$$

Hence, the principal oxidation number of Cr is +3

- (ii) Coordination number = $2 \times 1 + 4 \times 1 = 6$
 Since both ammine and bromo are monodentate ligands

- (iii) sp^3d^2 hybridization
 (iv) Bond angle of 90°
 (v) The geometry is octahedral



(vi) $E.A.N = 78 - 4 + (2 \times 6) = 78 - 4 + 12 = 86$

- (vii) The electron configuration of Pt^{4+} is $[Xe] 4f^{14} 5d^6$

Number of electrons from d - subshell = 6

Number of electrons from ligands = $2 \times 6 = 12$

Total electrons = $6 + 12 = 18$

The complex ion is stable according to E.A.N. rule since the total electrons is equal to 18

- (e) $[Mn(CO)_5]$

- (i) Let the oxidation number of manganese be M ;

$$M + 5(0) = 0$$

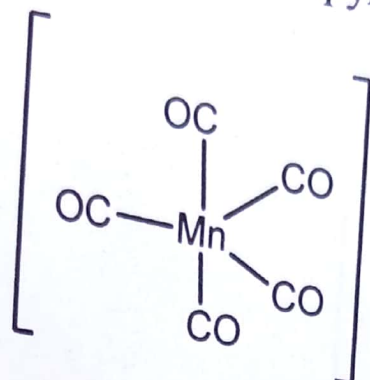
$$P + 0 = 0$$

$$P = 0$$

Hence, the principal oxidation number of Mn is 0

- (ii) Coordination number = $5 \times 0 = 0$
 Since carbonyl is a monodentate ligand

- (iii) sp^3d hybridization
- (iv) Bond angle of 90° & 120°
- (v) The geometry is trigonal bipyramidal



(vi) $E.A.N = 25 - 0 + (2 \times 6) = 25 - 0 + 12 = 37$

(vii) The electron configuration of Mn is $[Ar] 4s^2 3d^5$

Number of electrons from d - subshell = 5

Number of electrons from ligands = $2 \times 6 = 12$

Total electrons = $5 + 12 = 17$

The complex is unstable according to E.A.N. rule since the total electrons is less than 18

(f) $[Co(en)_2(C_2O_4)]^+$

(i) Let the oxidation number of cobalt be C ;

$C + 2(0) - 2 = +1$ (ethylene diamine is a neutral ligand while oxalate has a charge of -2)

$$C + 0 - 2 = +1$$

$$C = +1 + 2 = +3$$

Hence, the principal oxidation number of Co is +3

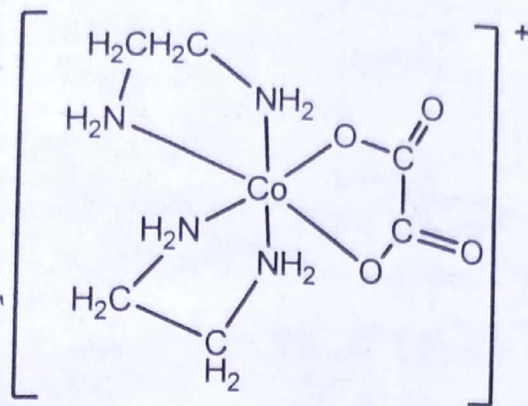
(ii) Coordination number = $2 \times 2 + 1 \times 2 = 6$

Since both ethylene diamine and oxalato are monodentate ligand

(iii) sp^3d^2 hybridization

(iv) Bond angle of 90°

(v) The geometry is octahedral



(vi) $E.A.N = 27 - 3 + (2 \times 6) = 24 - 0 + 12 = 36$

(vii) The electron configuration of Co is $[\text{Ar}] 3d^6$

Number of electrons from d - subshell = 6

Number of electrons from ligands = $2 \times 6 = 12$

Total electrons = $6 + 12 = 18$

The complex ion is stable according to E.A.N. rule since the total electrons is 18

(g) $[\text{Ni}(\text{H}_2\text{O})_4](\text{NO}_3)_2$

(i) Let the oxidation number of nickel be N;

$$N + 4(0) + 2(-1) = 0$$

$$P + 0 - 2 = 0$$

$$P = +2$$

Hence, the principal oxidation number of Ni is +2

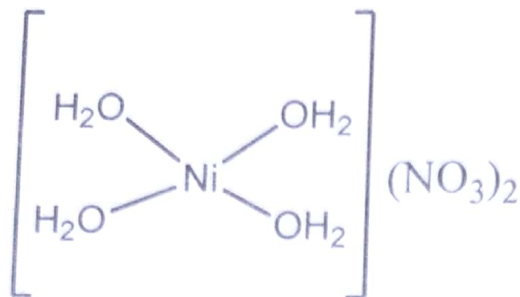
(ii) *Coordination number = $4 \times 1 = 4$*

Since nitrate is a monodentate ligand

(iii) sp^2d hybridization

(iv) Bond angle of 120°

(v) The geometry is square planar



(vi) $E.A.N = 28 - 2 + (2 \times 4) = 28 - 2 + 12 = 36$

(vii) The electron configuration of Ni^{2+} is $[\text{Ne}] 3d^8$

Number of electrons from d - subshell = 8

Number of electrons from ligands = $2 \times 6 = 12$

Total electrons = $8 + 12 = 20$

The complex is unstable according to E.A.N. rule since the total electrons is greater than 18

12.2 Rules for Naming Complexes

1. In case of salts, name the cation first and then the anion e.g $\text{K}_2[\text{Ni}(\text{CN})_4]$.

2K^+ and

[cation]

$[\text{Ni}(\text{CN})_4]^{2-}$

[anion]

2. In any complex ion or neutral molecule, name the ligand first and then the metal e.g

$[\text{Ni}(\text{CN})_4]^{2-}$ = tetracyano nickelate (II) ion;

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ = hexaaqua iron (II) ion

3. If there is more than one type of ligand in the complex, then, name them in alphabetical order and negative ligands must be named first e.g $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]^{2+}$ the ligands are named dicyano diammine; $[\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$ the ligands are named triammine triaquo

4. End the name of negative ligands with letter "o", but give neutral ligands the name of the ligand. E.g ammine for NH_3 and iodo for I^- .
5. Denote the number of a particular type with prefix di- for two, tri- for three, tetra- for four e.t.c. For bidentate or polydentate ligands, use bis- for two, tris- for three, tetrakis- for four e.t.c.
6. If the complex is a cation, then use the ordinary name for the metal e.g $[\text{Fe}(\text{CO})_5]^{2+}$ is named penta carbony iron (II).
7. If the complex ion is an anion, then end the name of the metal with suffix -ate. When there is a Latin name for the metal, it is used to name the metal except for mercury.

Table 12.4: Examples of elements with Latin names and their complex anionic names

English Name	Latin Name	Complex Anionic Name
Copper	Cuprum	Cuprate
Gold	Aurum	Aurate
Iron	Ferrum	Ferrate
Silver	Argentum	Argentate

best explained by *Ligand field* and *Molecular orbital theories*.

12.3.2. Crystal Field Theory

Bethe and Van Vleck developed this theory. The attraction between the central metal and ligands in a complex is considered purely electrostatic. The transition metal is considered positively charged, equal to the oxidation state. This is surrounded by negatively charged or neutral ligands with electron pair(s). For neutral ligands such as H_2O , the negative end of the dipole in the molecule ($\text{O}^{\delta-}$) is directed towards the metal ion. The electron on the central metal are under repulsive forces from those of the ligands. The assumptions of the crystal field theory are as follows:

- Ligands are treated as point charges
- There are no attraction between orbitals of metals and those of the ligands
- The d -orbital on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroyed the degeneracy of these orbitals, i.e. that is the orbitals now have different energies.

12.3.3 Molecular Orbital Theory

This theory fully allowed contributions from both covalent and ionic bonds. However, the theory is the most important approach to chemical bonding; it has not displaced the other theories. This is because the quantitative calculations involved are difficult and

lengthy, involving the use of extensive computer time. Much of the qualitative description can be obtained by other approaches using symmetry and group theory.

12.4 Isomerism of Octahedral and Square Planar Complexes

Isomerism is the existence of a molecule/ complex or ion in the same molecular formula but different arrangement of ligands. Such complexes are called ISOMERS. There are two types of isomerism; *structural isomerism and stereoisomerism*.

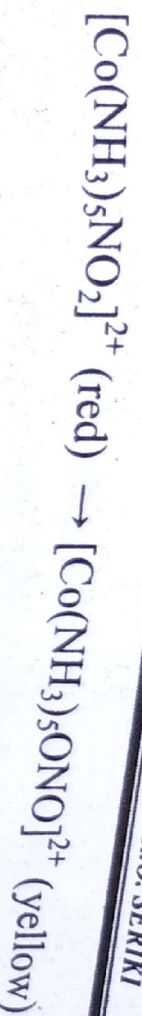
1. Structural Isomers

These isomers differ in how the atoms are joined together, that is, in the order in which they are linked together. Various structural isomers are:

A. Hydration Isomers

These are isomers that differ in the number of water molecules in and out of the coordination sphere. Many metal complexes are prepared by reactions carried out in aqueous solutions. Consequently, solid complexes are frequently obtained as hydrates. Water is also a potential ligand, so various possibilities exist for compounds to be prepared with water held in both ways. For instance, the compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ [chromium (III) chloride hexahydrate], a normal salt, has 4 important hydrated isomers.

- I. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ - Hexaaqua chromium (III) chloride (violet colour)
- II. $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ - Chloro pentaqua chromium (III) chloride monohydrate (pale green)
- III. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ - Dichloro tetraqua chromium (III) chloride dihydrate (dark green)
- IV. $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ - Trichloro triqua chromium (III) trihydrate



Other examples are:

- $[\text{Ni}(\text{SCN})_4]^{2-}$ = Thiocyanato nickelate (II) ion {Linked through sulphur} and
- $[\text{Ni}(\text{NCS})_4]^{2-}$ = Tetraisothiocyanato nickelate (II) ion {Linked through nitrogen}

E. Coordination Isomers

These are isomers whereby the ligands are exchanged between two metal atoms in a coordination sphere. It refers to cases where there are different ways to arrange several ligands around two metal centers. Examples of coordination isomers are:

- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ = hexammine cobalt (III) hexacyano chromate (III) and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ = hexammine chromium (III) hexacyano cobaltate (III)
- $[\text{Cu}(\text{en})_2][\text{PtBr}_4]$ = bis-ethylenediamine copper (II) tetrabromo platinate (II) and $[\text{Pt}(\text{en})_2][\text{CuBr}_4]$ = bis-ethylenediamine platinum (II) tetrabromo cuprate (II)
- $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ = tetraammine platinum (II) hexachloro platinate (IV) and $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$ = dichloro tetraammine platinum (IV) tetrachloro platinate (II)

2. Stereoisomer

Stereoisomers are divided into two major types; geometric and optical isomers.

A. Geometric Isomers

These are isomers, which differ in the special orientation of ligands in the coordination sphere. If the two similar ligands are parallel to each other in the complex, it is called the *cis*- isomer and when they are perpendicular to each other, it is called the

