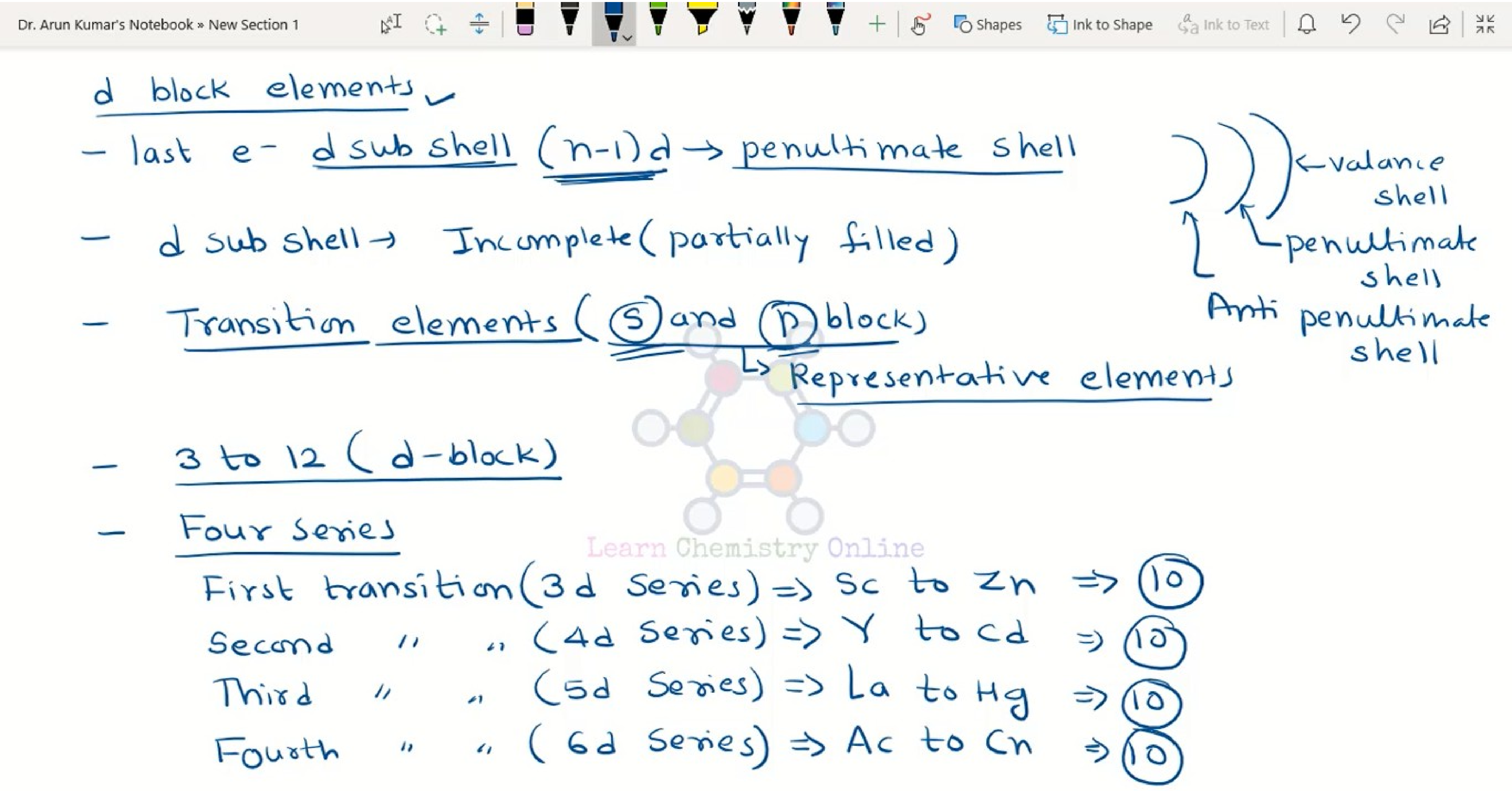
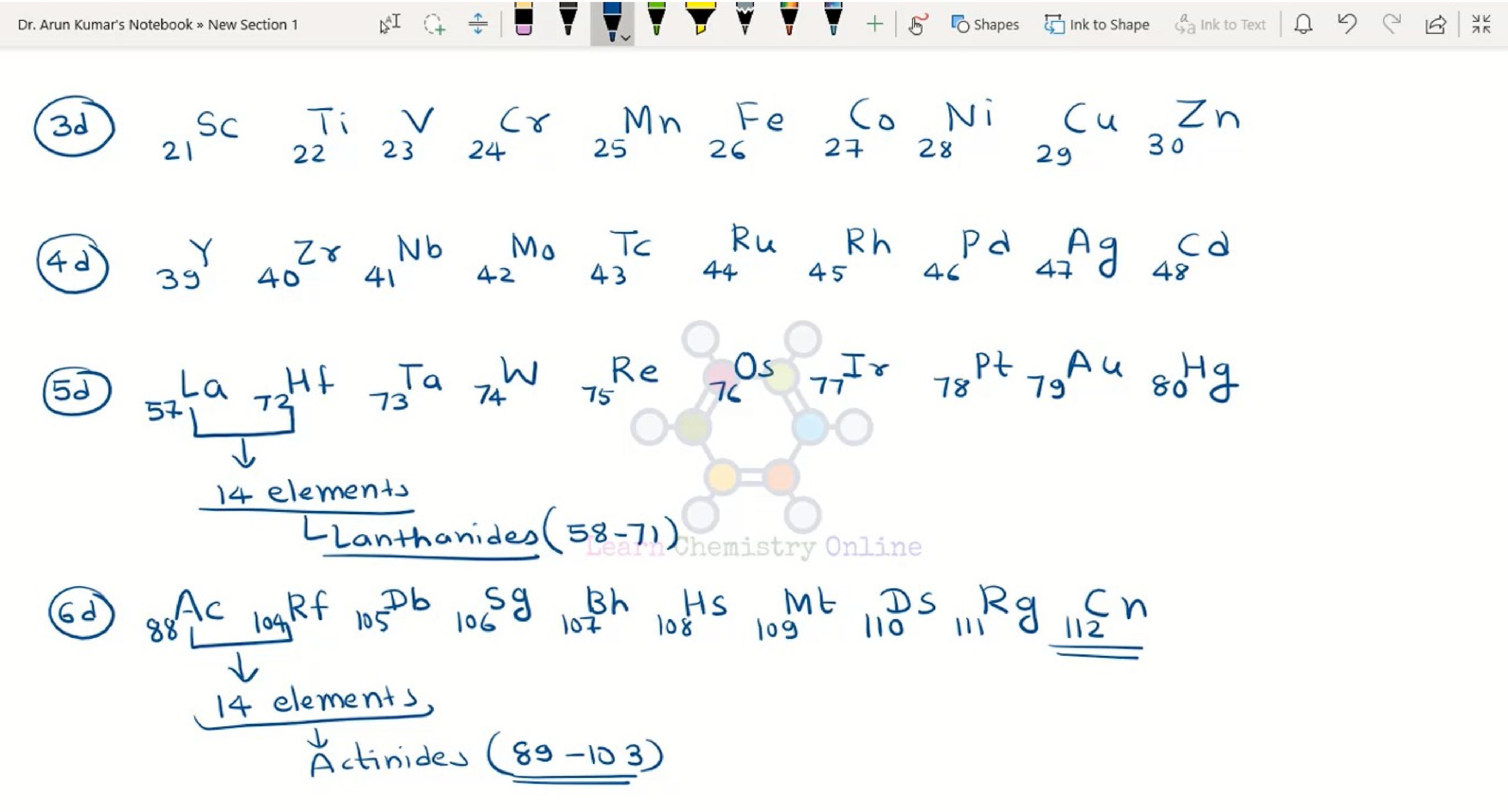


d block elements ✓

- last e- d sub shell $(n-1)d$ → penultimate shell
- d sub shell → Incomplete (partially filled)
- Transition elements (Ⓢ and Ⓟ block)
  ↳ Representative elements
- 3 to 12 (d-block)
- Four series

First transition (3d Series) ⇒ Sc to Zn ⇒ ⑩
Second " " (4d Series) ⇒ Y to Cd ⇒ ⑩
Third " " (5d Series) ⇒ La to Hg ⇒ ⑩
Fourth " " (6d Series) ⇒ Ac to Cn ⇒ ⑩

←valance shell
penultimate shell
Anti penultimate shell



③d $_{21}Sc$ $_{22}Ti$ $_{23}V$ $_{24}Cr$ $_{25}Mn$ $_{26}Fe$ $_{27}Co$ $_{28}Ni$ $_{29}Cu$ $_{30}Zn$

④d $_{39}Y$ $_{40}Zr$ $_{41}Nb$ $_{42}Mo$ $_{43}Tc$ $_{44}Ru$ $_{45}Rh$ $_{46}Pd$ $_{47}Ag$ $_{48}Cd$

⑤d $_{57}La$ $_{72}Hf$ $_{73}Ta$ $_{74}W$ $_{75}Re$ $_{76}Os$ $_{77}Ir$ $_{78}Pt$ $_{79}Au$ $_{80}Hg$

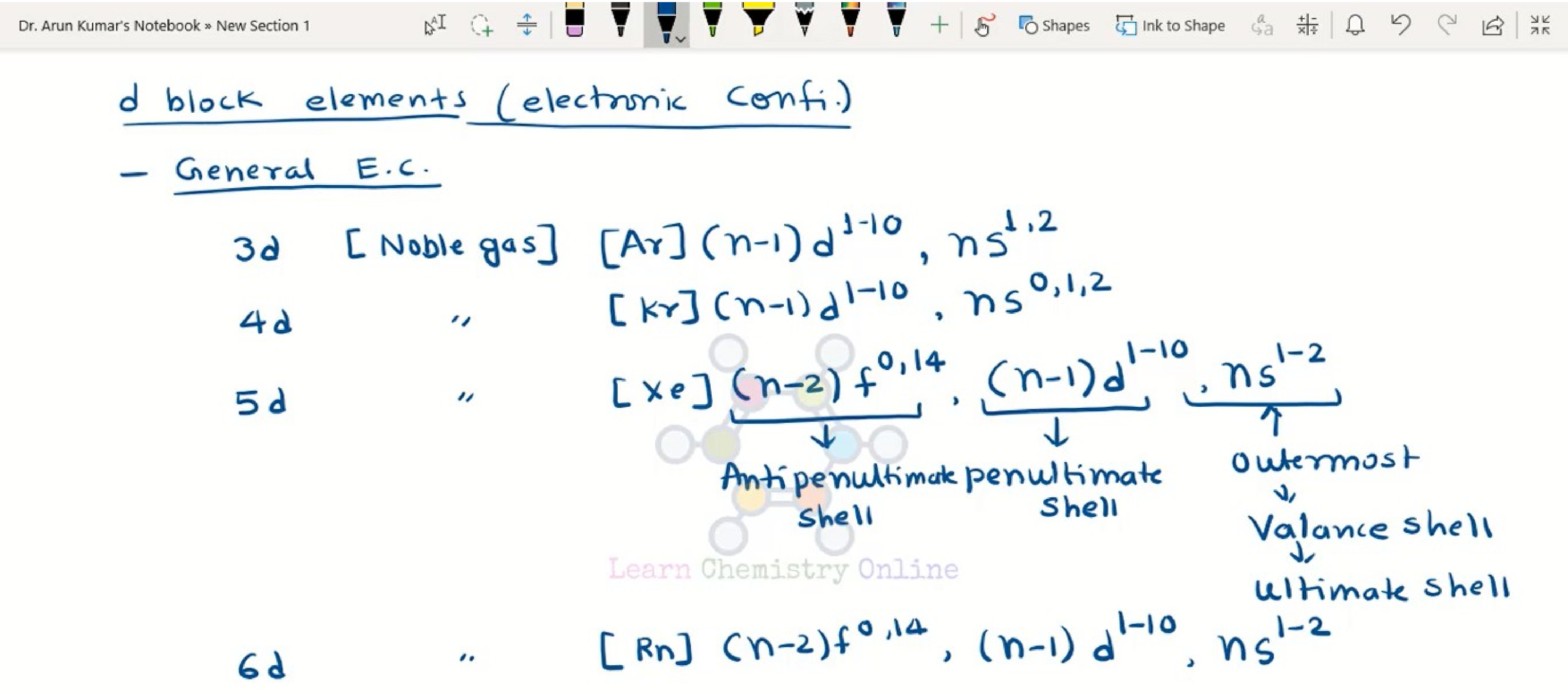
14 elements

Lanthanides (58-71)

⑥d $_{88}Ac$ $_{104}Rf$ $_{105}Db$ $_{106}Sg$ $_{107}Bh$ $_{108}Hs$ $_{109}Mt$ $_{110}Ds$ $_{111}Rg$ $_{112}Cn$

14 elements

Actinides (89 -103)



d block elements (electronic confi.)

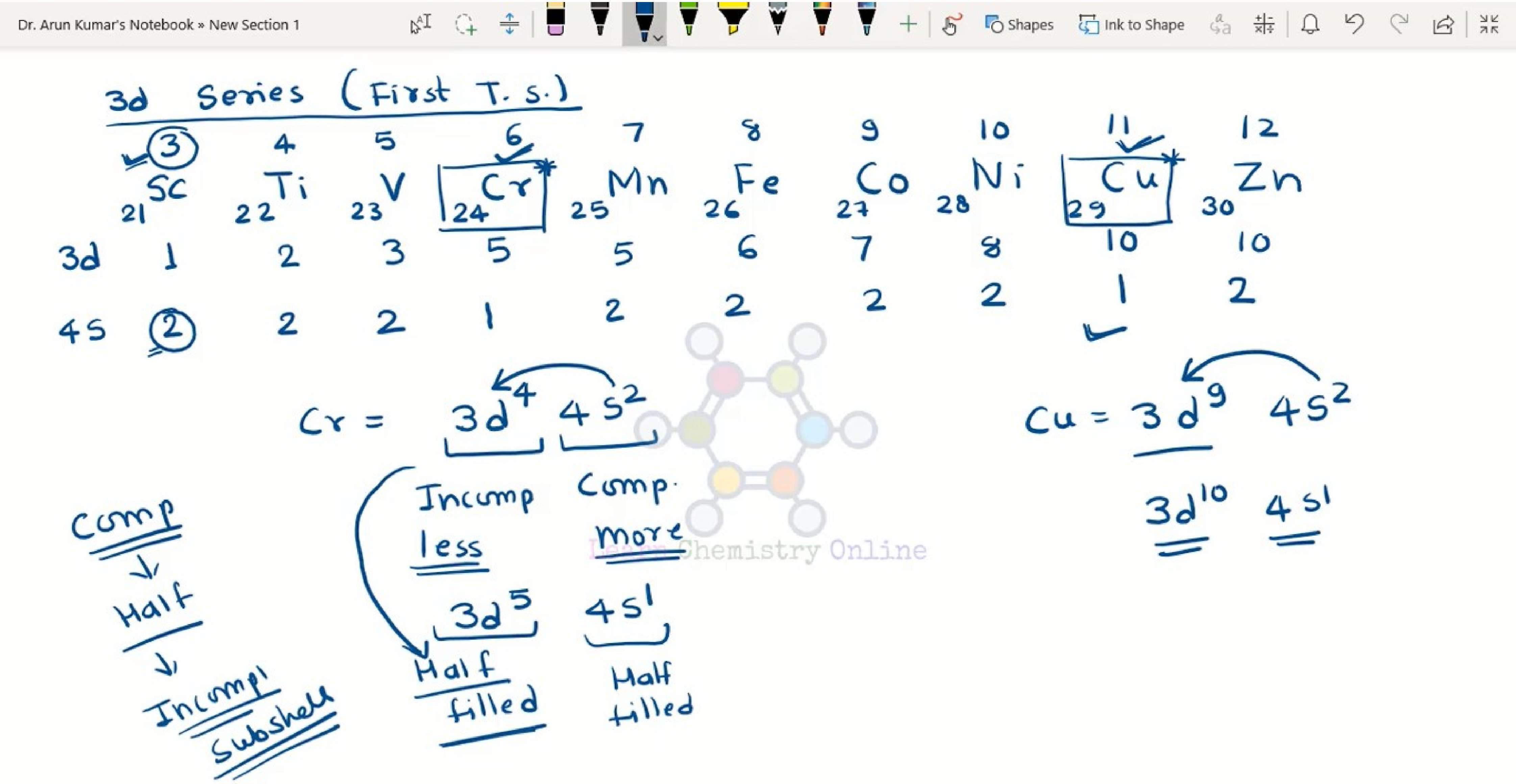
– General E.C.

3d [Noble gas] $[Ar](n-1)d^{1-10}, ns^{1,2}$

4d 〃 $[Kr](n-1)d^{1-10}, ns^{0,1,2}$

5d 〃 $$[Xe]\underbrace{(n-2)f^{0,14}}_{\downarrow \text{ Antipenultimate shell}}, \underbrace{(n-1)d^{1-10}}_{\downarrow \text{ penultimate shell}}, \underbrace{ns^{1-2}}_{\uparrow \text{ Outermost} \downarrow \text{ Valance shell} \downarrow \text{ ultimate shell}}$$

6d 〃 $[Rn]\ (n-2)f^{0,14}, (n-1)\ d^{1-10}, ns^{1-2}$



3d Series (First T. s.)

	③	4	5	6	7	8	9	10	11	12
	$_{21}Sc$	$_{22}Ti$	$_{23}V$	$\boxed{_{24}Cr}$ *	$_{25}Mn$	$_{26}Fe$	$_{27}Co$	$_{28}Ni$	$\boxed{_{29}Cu}$ *	$_{30}Zn$
3d	1	2	3	5	5	6	7	8	10	10
4s	②	2	2	1	2	2	2	2	1	2

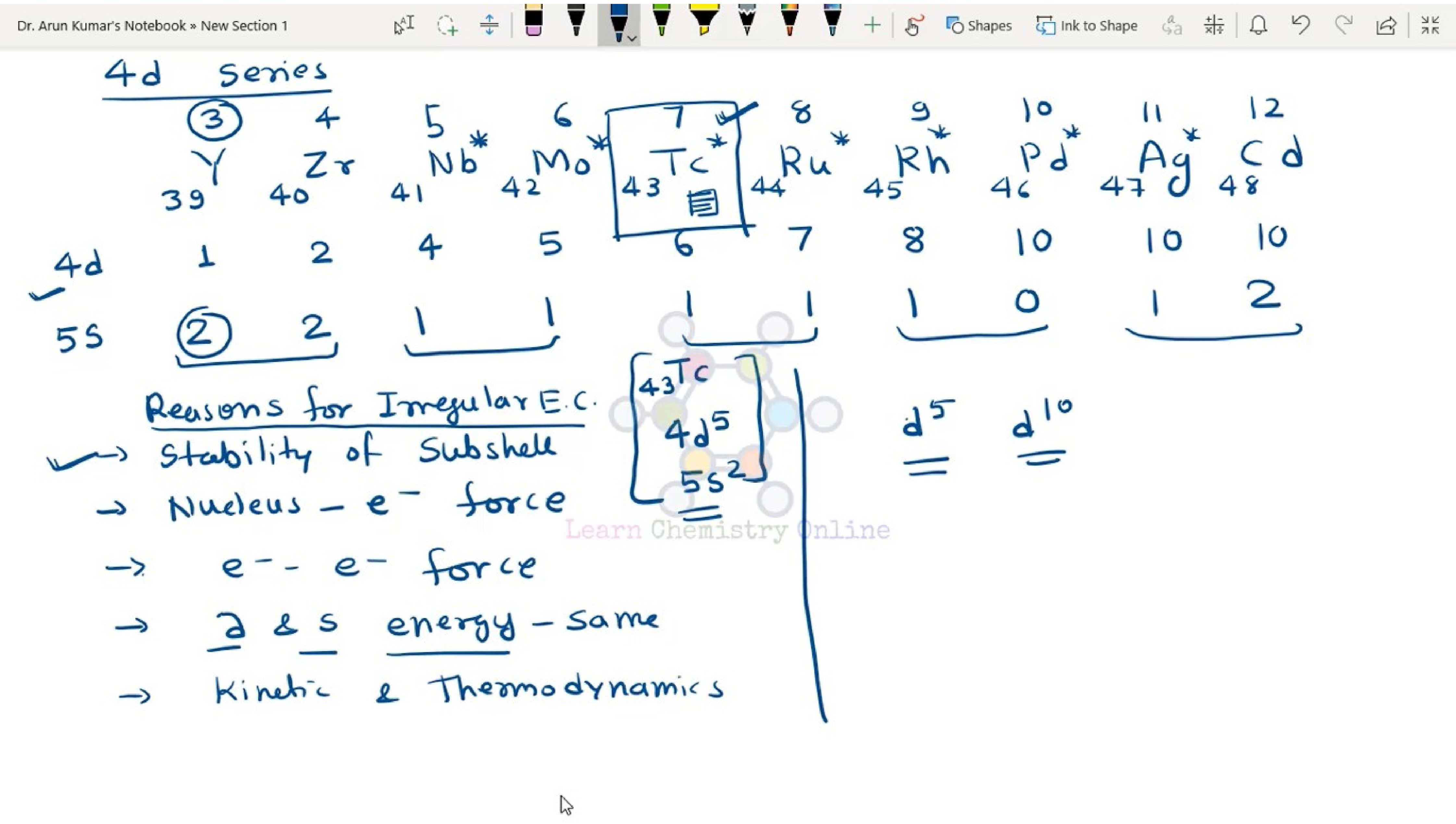
$$Cr = \underbrace{3d^4}_{\text{Incump less}}\ \underbrace{4s^2}_{\text{Comp. more}}$$

$$\underbrace{3d^5}_{\text{Half filled}}\ \underbrace{4s^1}_{\text{Half filled}}$$

$$Cu = \underline{3d^9}\ 4s^2$$

$$\underline{\underline{3d^{10}}}\ \underline{\underline{4s^1}}$$

Comp
↓
Half
↓
Incumpl Subshell



4d series

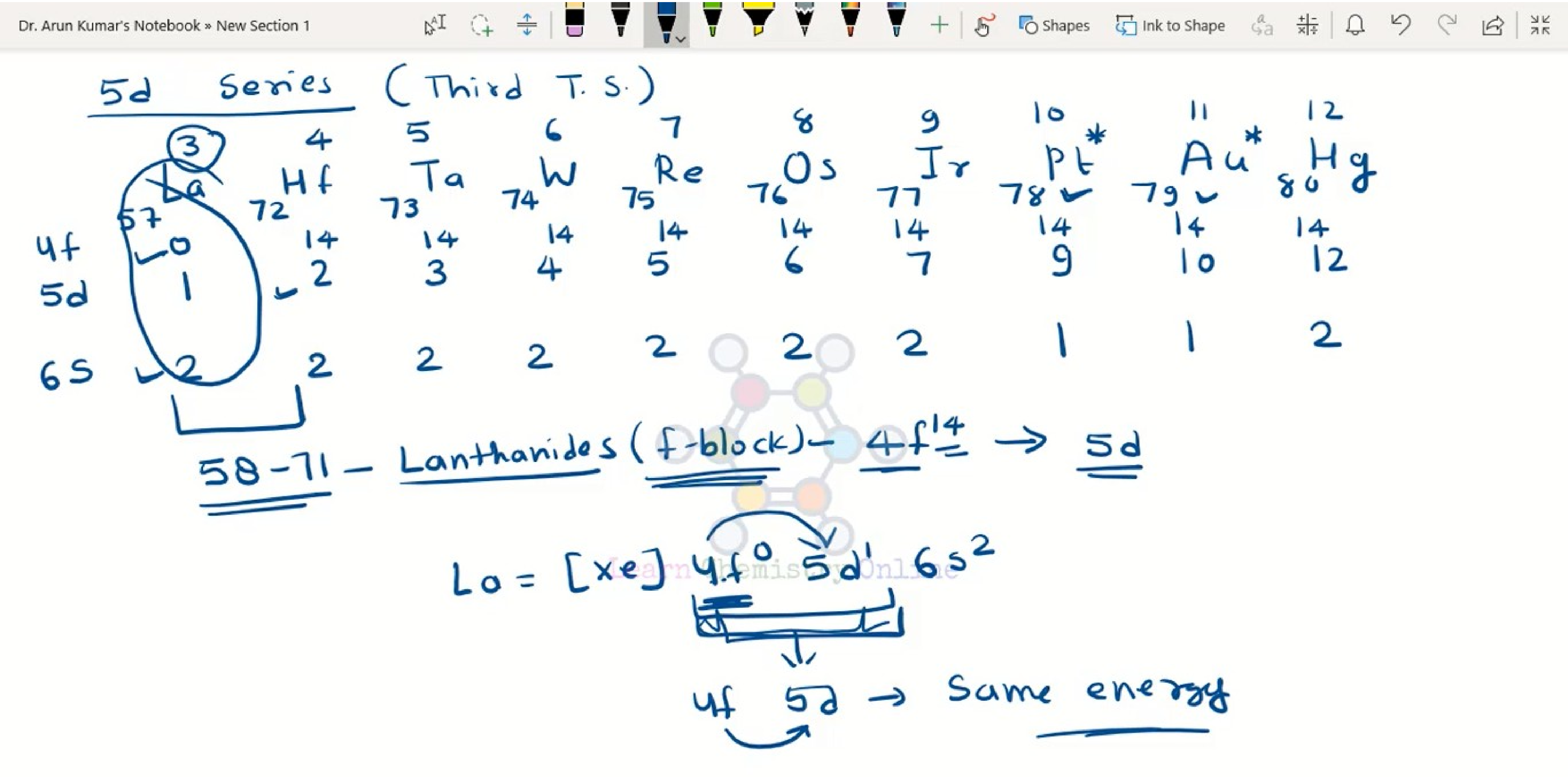
	③	4	5	6	7	8	9	10	11	12
	$_{39}Y$	$_{40}Zr$	$_{41}Nb^*$	$_{42}Mo^*$	$_{43}Tc^*$	$_{44}Ru^*$	$_{45}Rh^*$	$_{46}Pd^*$	$_{47}Ag^*$	$_{48}Cd$
4d	1	2	4	5	6	7	8	10	10	10
5s	②	2	1	1	1	1	1	0	1	2

$_{43}Tc$
$\underline{\underline{4d^5\ 5s^2}}$

$\underline{\underline{d^5}}$ $\underline{\underline{d^{10}}}$

Reasons for Irregular E.C.

→ Stability of Subshell
→ Nucleus – e^- force
→ e^- – e^- force
→ d & s energy – same
→ Kinetic & Thermodynamics



5d Series (Third T. S.)

	3	4	5	6	7	8	9	10	11	12
	$_{57}$~~La~~	$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt*	$_{79}$Au*	$_{80}$Hg
4f	0	14	14	14	14	14	14	14	14	14
5d	1	2	3	4	5	6	7	9	10	12
6s	2	2	2	2	2	2	2	1	1	2

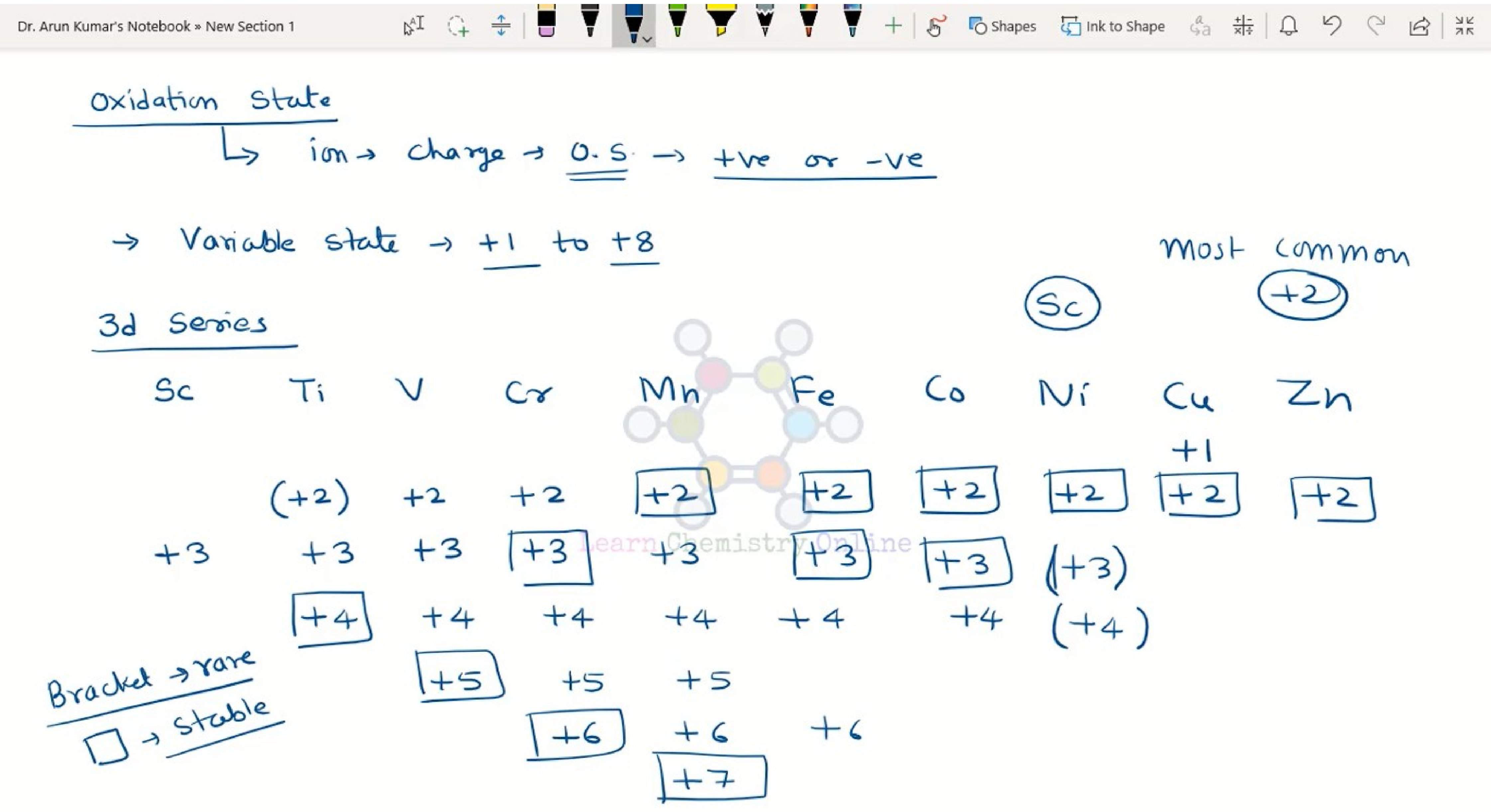
58-71 – Lanthanides (f-block) – $4f^{14}$ → 5d

La = [Xe] $4f^0\ 5d^1\ 6s^2$

4f 5d → Same energy

6d series (4 T.S.)

	③	4	5	6	7	8	9	10	11	12
	$_{88}Ac$	$_{104}Rf$	$_{105}Db$	$_{106}Sg$	$_{107}Bh$	$_{108}Hs$	$_{109}Mt$	$_{110}Ds$	$_{111}Rg$ ⊛	$_{112}Cn$
5f	0	14	14	14	14	14	14	14	14	14
6d	1	2	3	4	5	6	7	8	10	10
7s	2	2	2	2	2	2	2	2	1	2



Oxidation State
↳ ion → charge → O.S. → +ve or -ve

→ Variable state → +1 to +8

most common

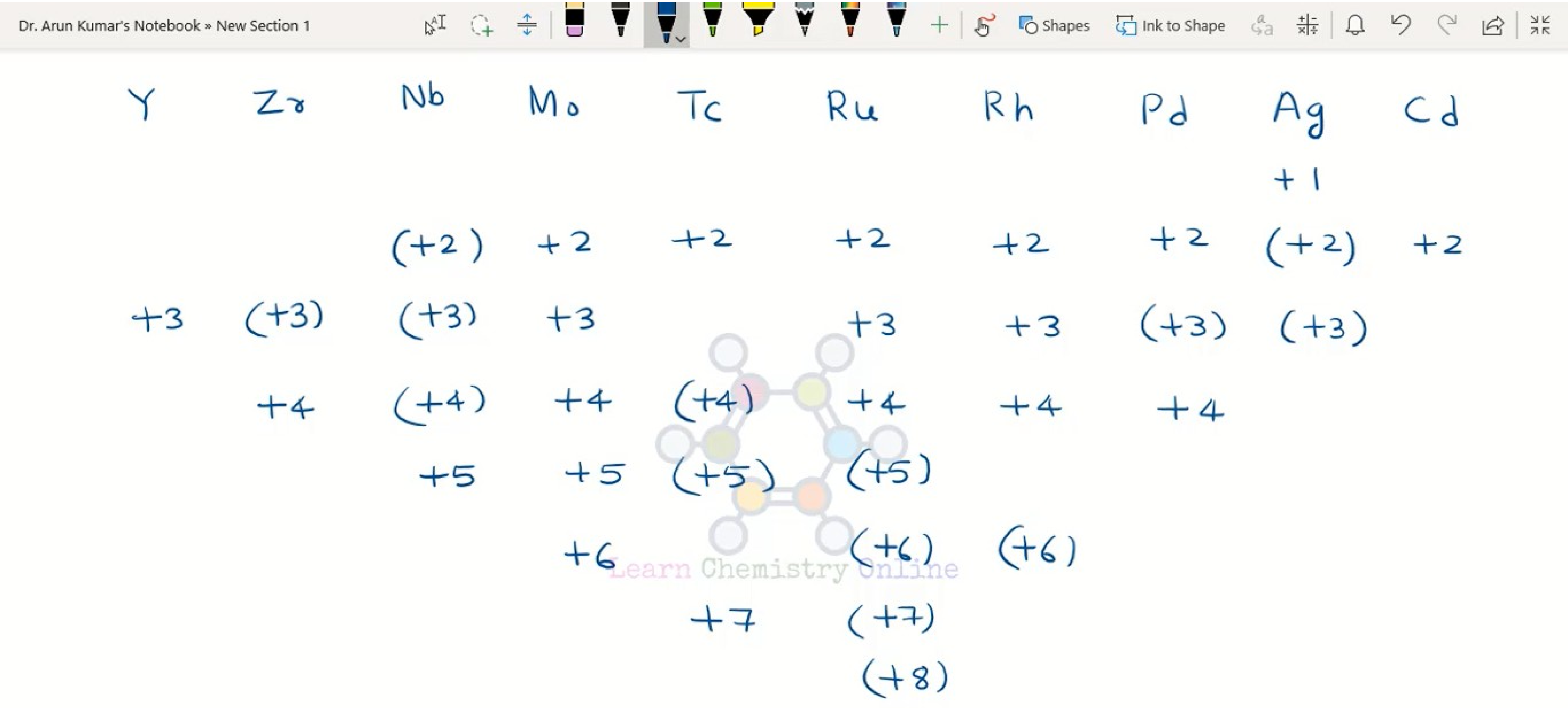
Sc

+2

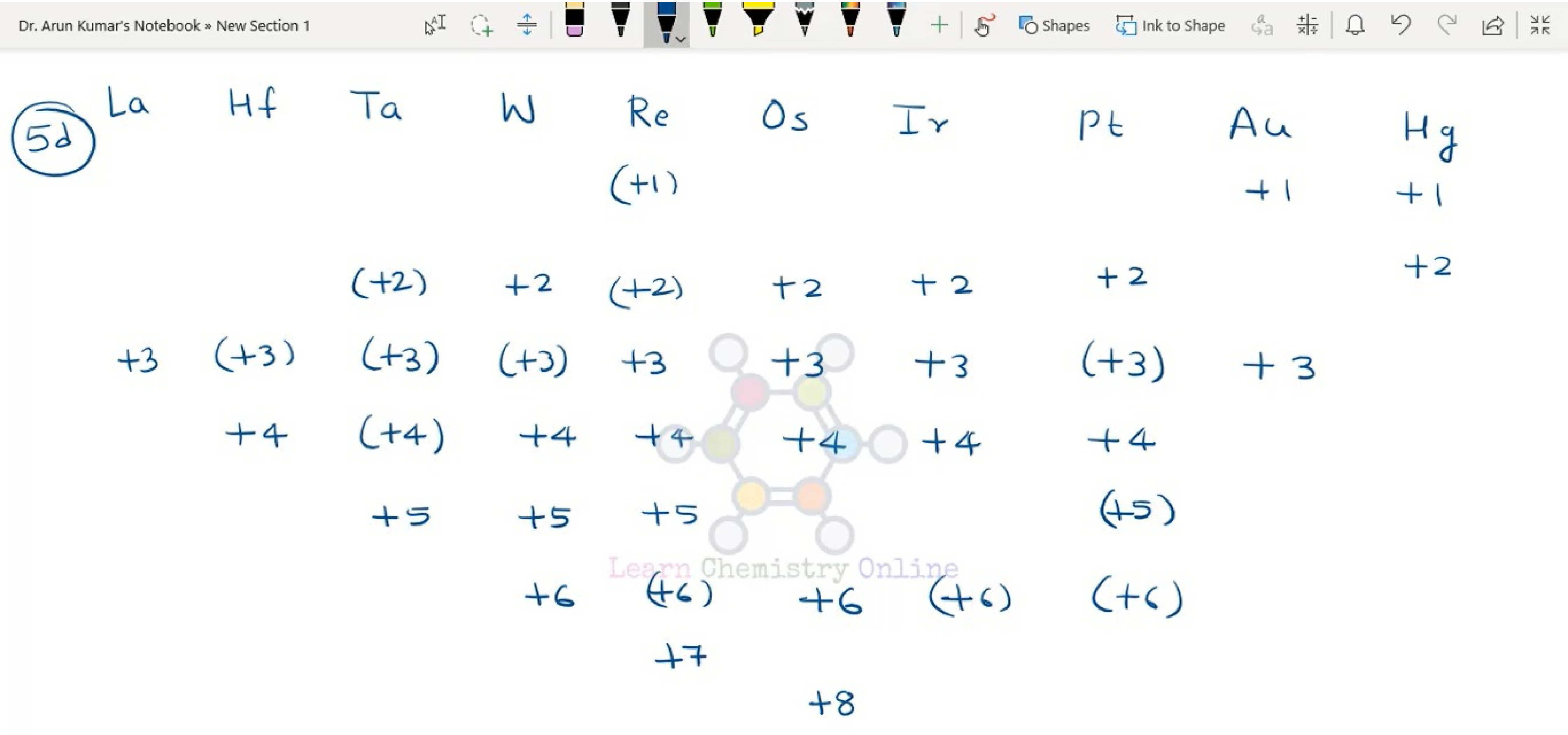
3d Series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	(+2)	+2	+2	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$
+3	+3	+3	$\boxed{+3}$	+3	$\boxed{+3}$	$\boxed{+3}$	(+3)		
	$\boxed{+4}$	+4	+4	+4	+4	+4	(+4)		
		$\boxed{+5}$	+5	+5					
			$\boxed{+6}$	+6	+6				
				$\boxed{+7}$					

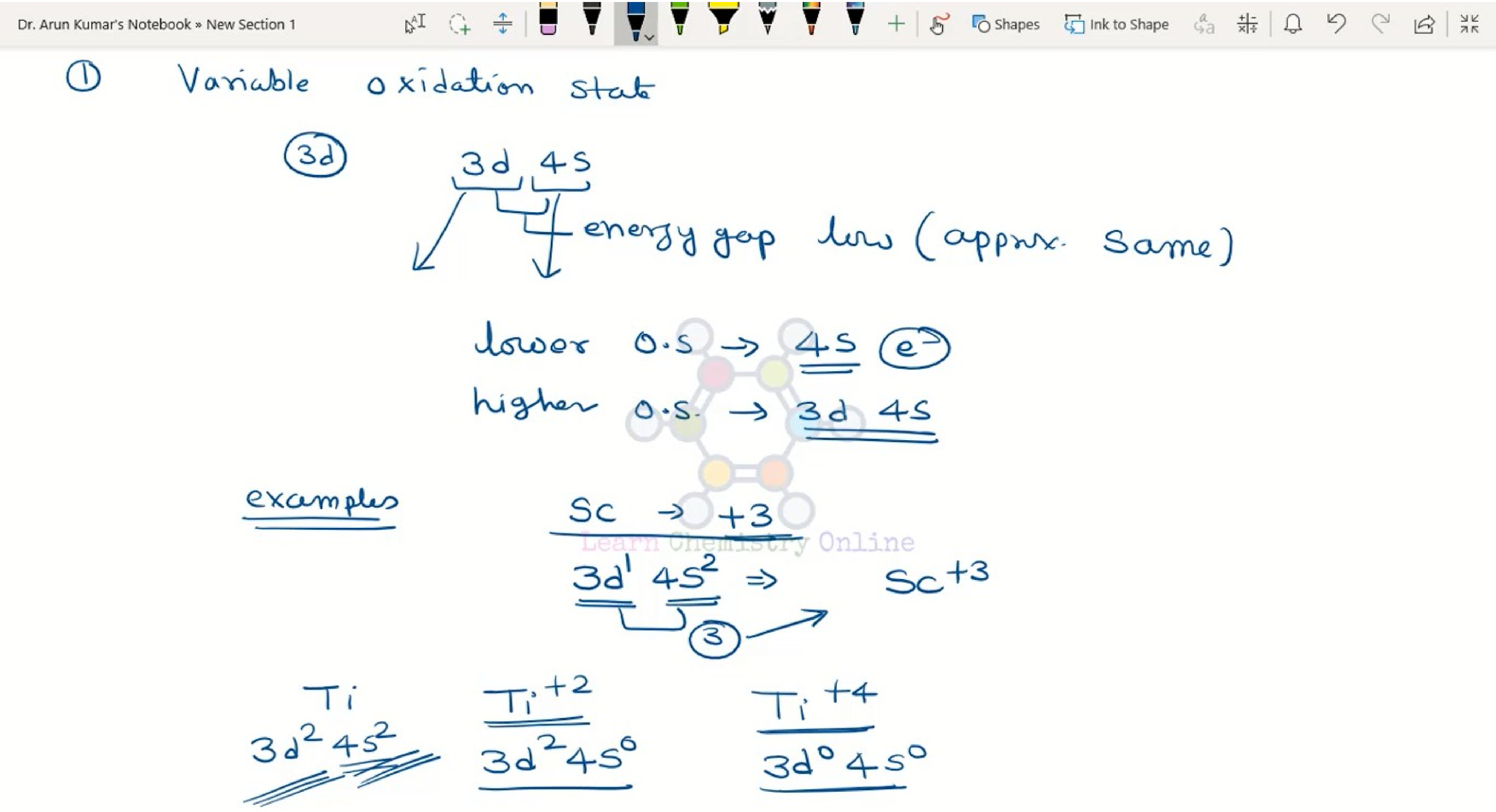
Bracket → rare
□ → stable



Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
								+1	
		(+2)	+2	+2	+2	+2	+2	(+2)	+2
+3	(+3)	(+3)	+3		+3	+3	(+3)	(+3)	
	+4	(+4)	+4	(+4)	+4	+4	+4		
		+5	+5	(+5)	(+5)				
			+6		(+6)	(+6)			
				+7	(+7)				
					(+8)				



5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
					(+1)				+1	+1
			(+2)	+2	(+2)	+2	+2	+2		+2
	+3	(+3)	(+3)	(+3)	+3	+3	+3	(+3)	+3	
		+4	(+4)	+4	+4	+4	+4	+4		
			+5	+5	+5			(+5)		
				+6	(+6)	+6	(+6)	(+6)		
					+7					
						+8				



① Variable oxidation state

③d

$\underbrace{3d}\ \underbrace{4s}$ → energy gap low (approx. same)

lower O.S → 4s e^-

higher O.S. → 3d 4s

examples

Sc → +3

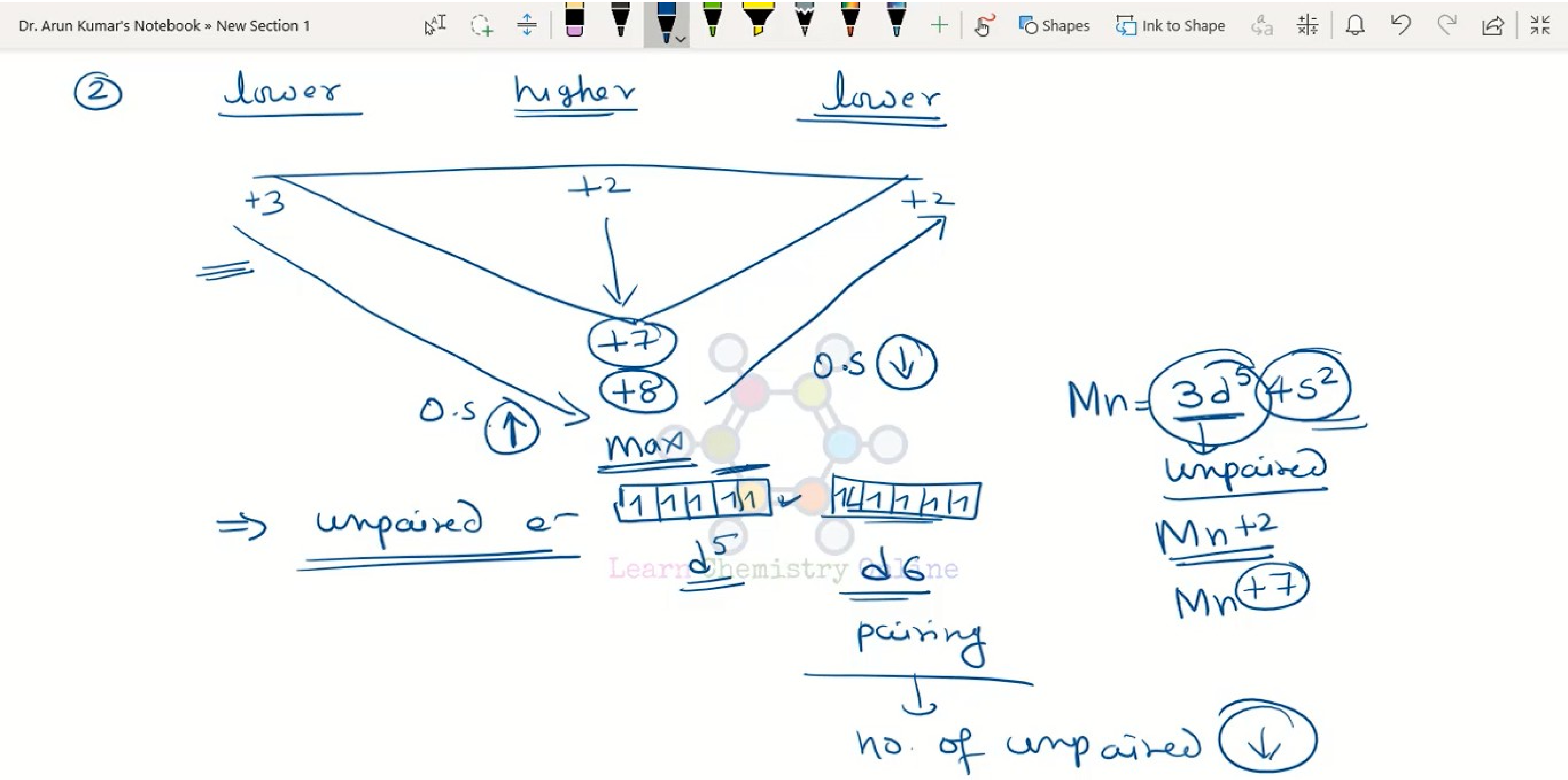
$3d^1\ 4s^2 \Rightarrow Sc^{+3}$

③

Ti
$3d^2 4s^2$

Ti^{+2}
$3d^2 4s^0$

Ti^{+4}
$3d^0 4s^0$



② lower higher lower

+3 +2 +2

+7

+8

0.S ↑

0.S ↓

max

d5 d6

⇒ unpaired e⁻

pairing

↓

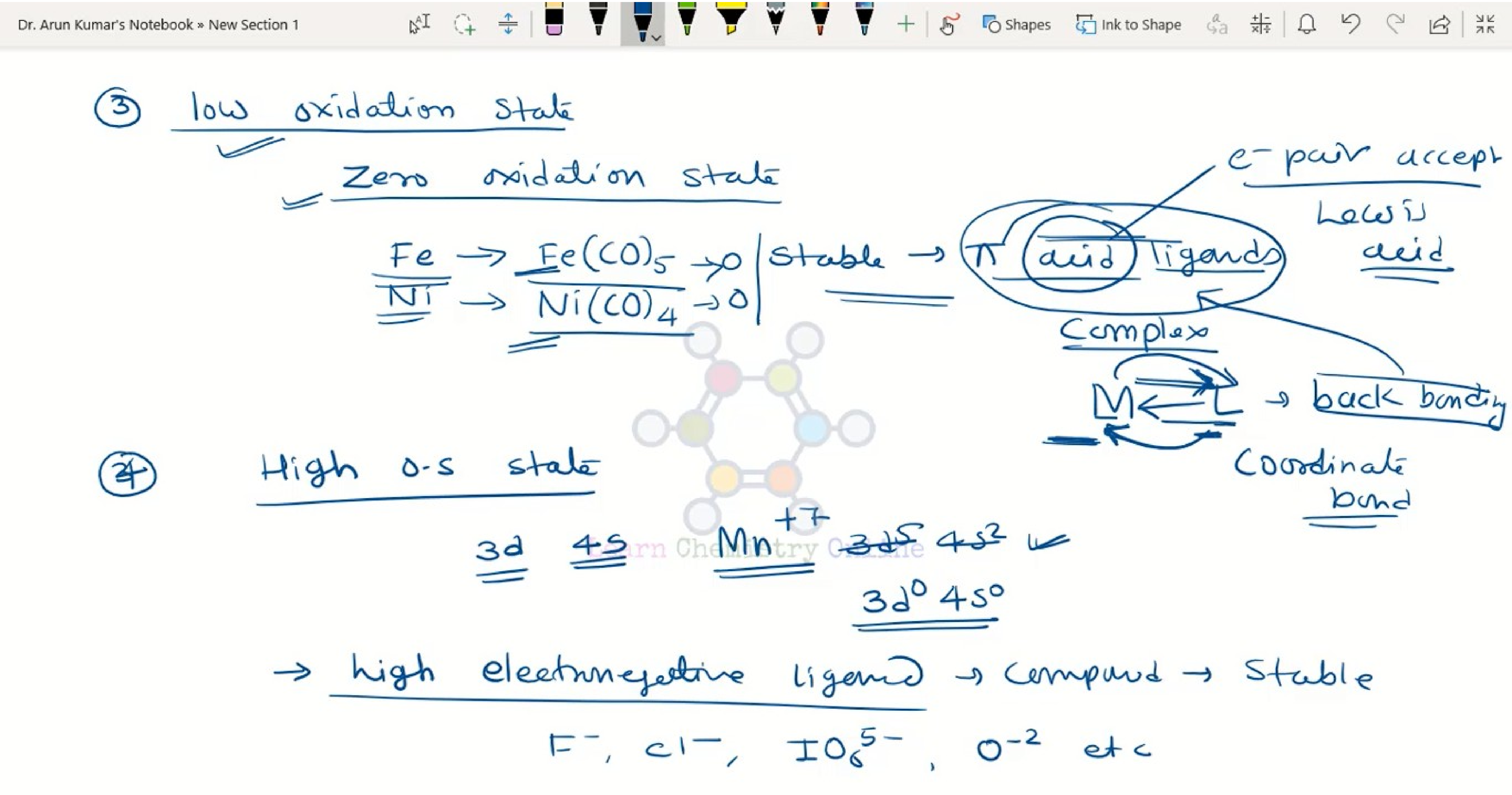
no. of unpaired ↓

$Mn = 3d^5 4s^2$

unpaired

Mn^{+2}

Mn^{+7}



③ low oxidation state

Zero oxidation state

$Fe \rightarrow Fe(CO)_5 \rightarrow 0$ | Stable → π acid ligands

$Ni \rightarrow Ni(CO)_4 \rightarrow 0$ |

e⁻ pair accept

Lewis acid

Complex

$M \rightleftarrows L$ → back bonding

Coordinate bond

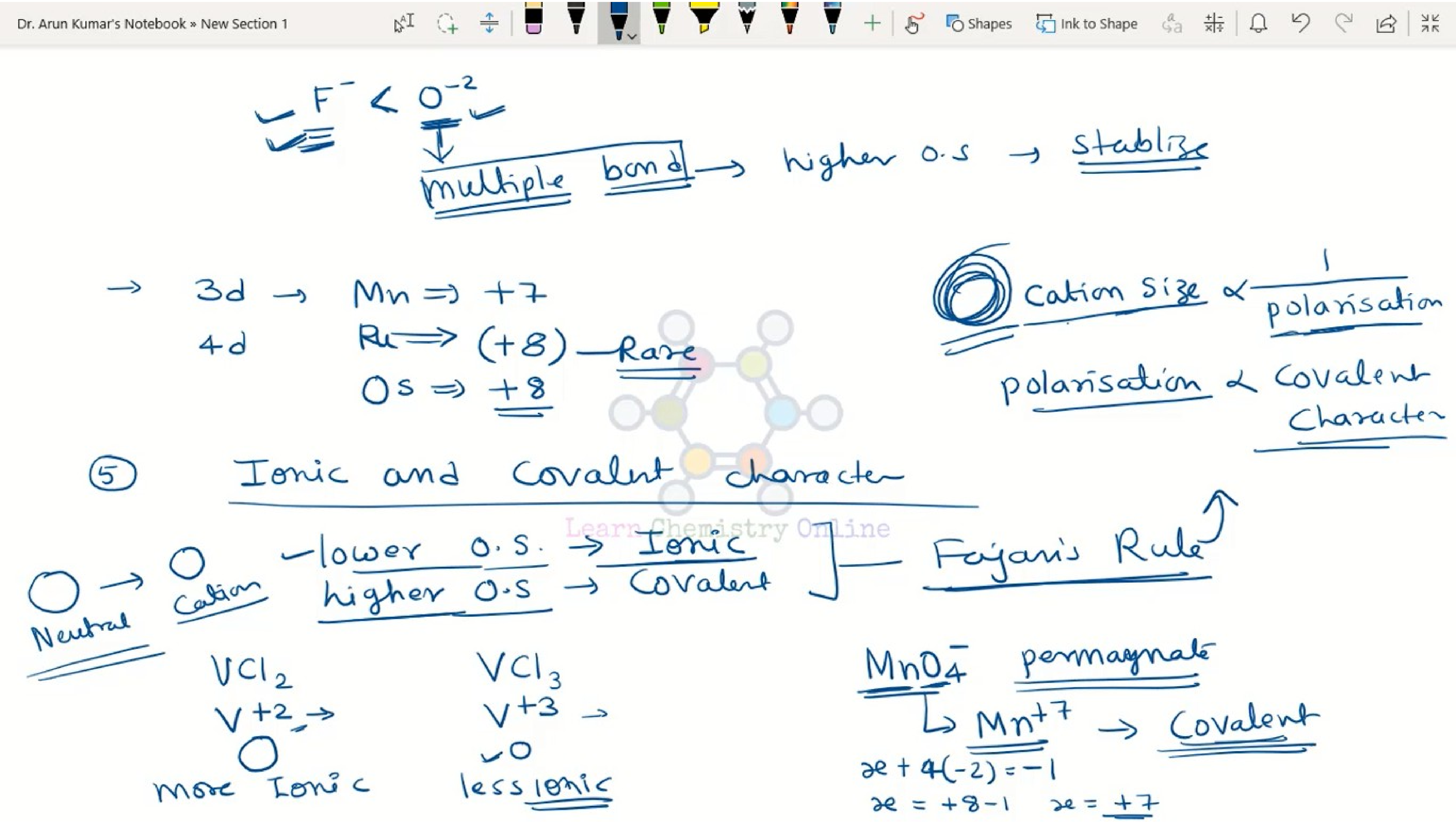
④ High o.s state

3d 4s Mn^{+7} ~~$3d^5$~~ $4s^2$

$3d^0 4s^0$

→ high electronegative ligand → compound → Stable

F^-, Cl^-, IO_6^{5-}, O^{-2} etc



✓ $F^- < O^{-2}$ ✓

↓

multiple bond → higher o.s → stablize

→ 3d → Mn ⇒ +7

4d Ru ⇒ (+8) — Rare

Os ⇒ +8

Cation size $\propto \frac{1}{\text{polarisation}}$

polarisation ∝ covalent character

⑤ Ionic and covalent character

Neutral → Cation

- lower O.S. → Ionic
- higher O.S → Covalent

] — Fajan's Rule

VCl_2 V^{+2} → more Ionic

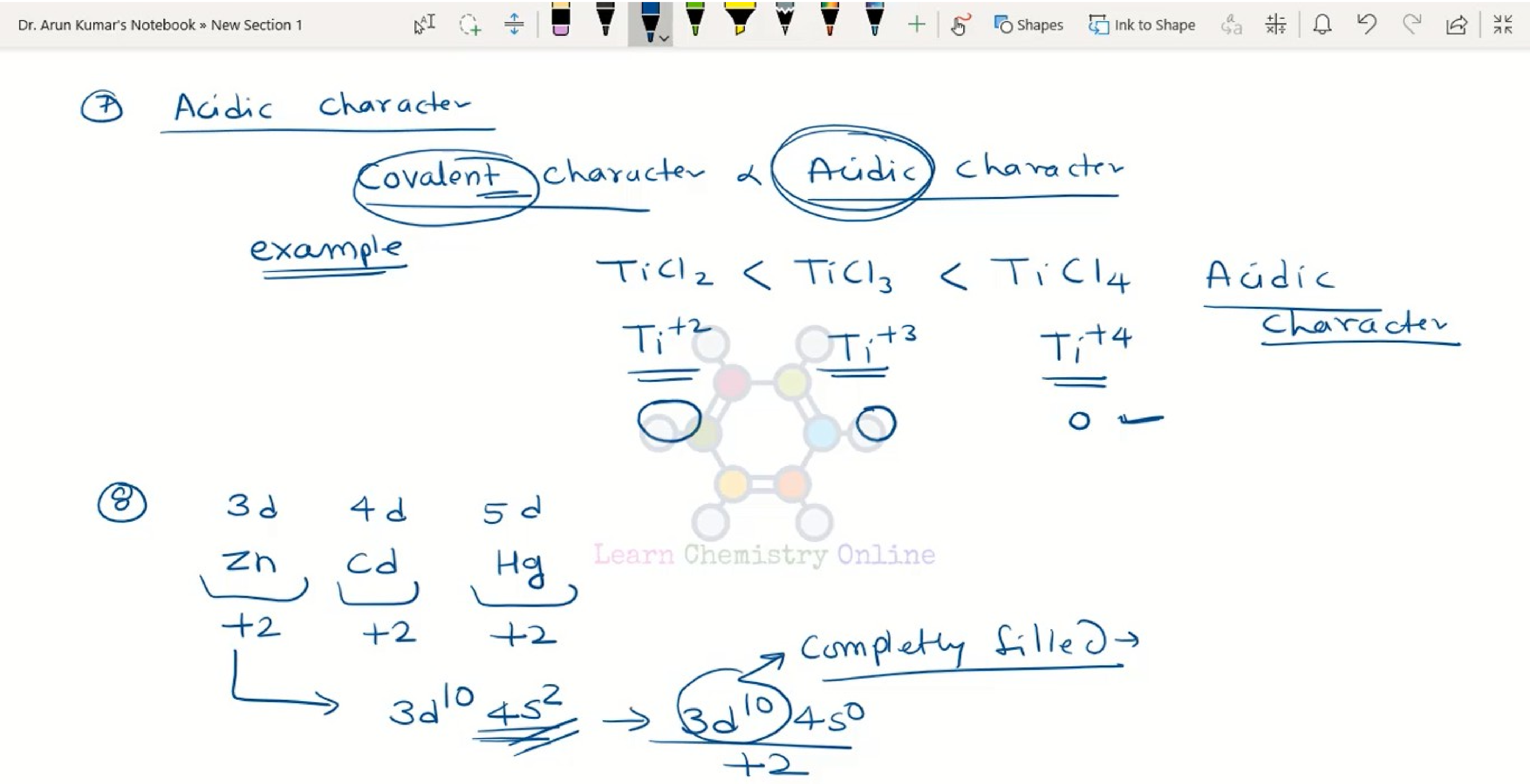
VCl_3 V^{+3} → less ionic

MnO_4^- permagnate

↳ Mn^{+7} → Covalent

$x + 4(-2) = -1$

$x = +8 - 1$ $x = +7$



⑦ Acidic character

Covalent character ∝ Acidic character

example

$TiCl_2 < TiCl_3 < TiCl_4$ Acidic character

Ti^{+2} Ti^{+3} Ti^{+4}

O O O

⑧ 3d 4d 5d

$\underbrace{Zn}_{+2}$ $\underbrace{Cd}_{+2}$ $\underbrace{Hg}_{+2}$

$\rightarrow 3d^{10}\cancel{4s^2} \rightarrow \underbrace{3d^{10}4s^0}_{+2}$

completly filled →

⑩ Relative stability of oxidation state

– nature of other elements

$\underline{\underline{d^0}}$ $\boxed{\underline{d^5}}$ $\underline{\underline{d^{10}}}$ → highly stable

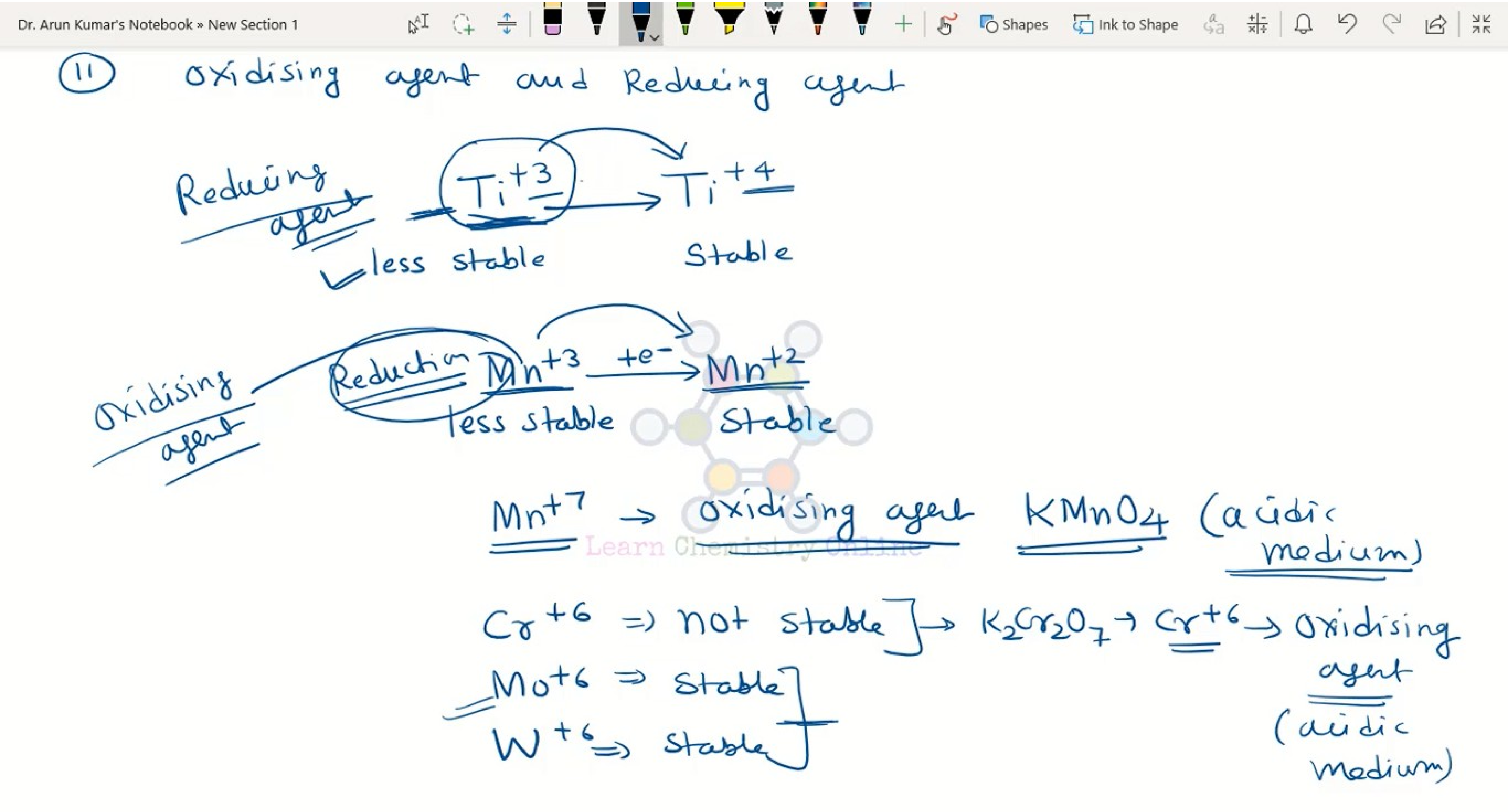
<u>example</u>

Ti ✓ Ti^{+3} < ✓ Ti^{+4} ✓

$3d^2 4s^2$ ✓ $3d^1 4s^0$ ✓ $\boxed{3d^0}$ $4s^0$

Mn^{+2} > Mn^{+3}

✓ $3d^5 4s^0$ $3d^4 4s^0$



⑪ Oxidising agent and Reducing agent

Reducing agent

$\text{Ti}^{+3} \longrightarrow \text{Ti}^{+4}$

less stable — Stable

Oxidising agent — Reduction

$\text{Mn}^{+3} \xrightarrow{+e^-} \text{Mn}^{+2}$

less stable — Stable

Mn^{+7} → oxidising agent $KMnO_4$ (acidic medium)

Cr^{+6} ⇒ not stable] → $K_2Cr_2O_7$ → Cr^{+6} → oxidising agent (acidic medium)

Mo^{+6} ⇒ stable

W^{+6} ⇒ stable

Magnetic properties

③ substance

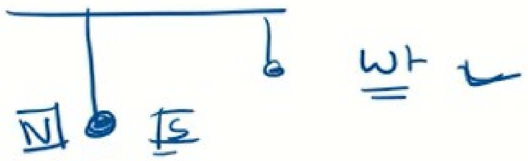
① paramagnetic

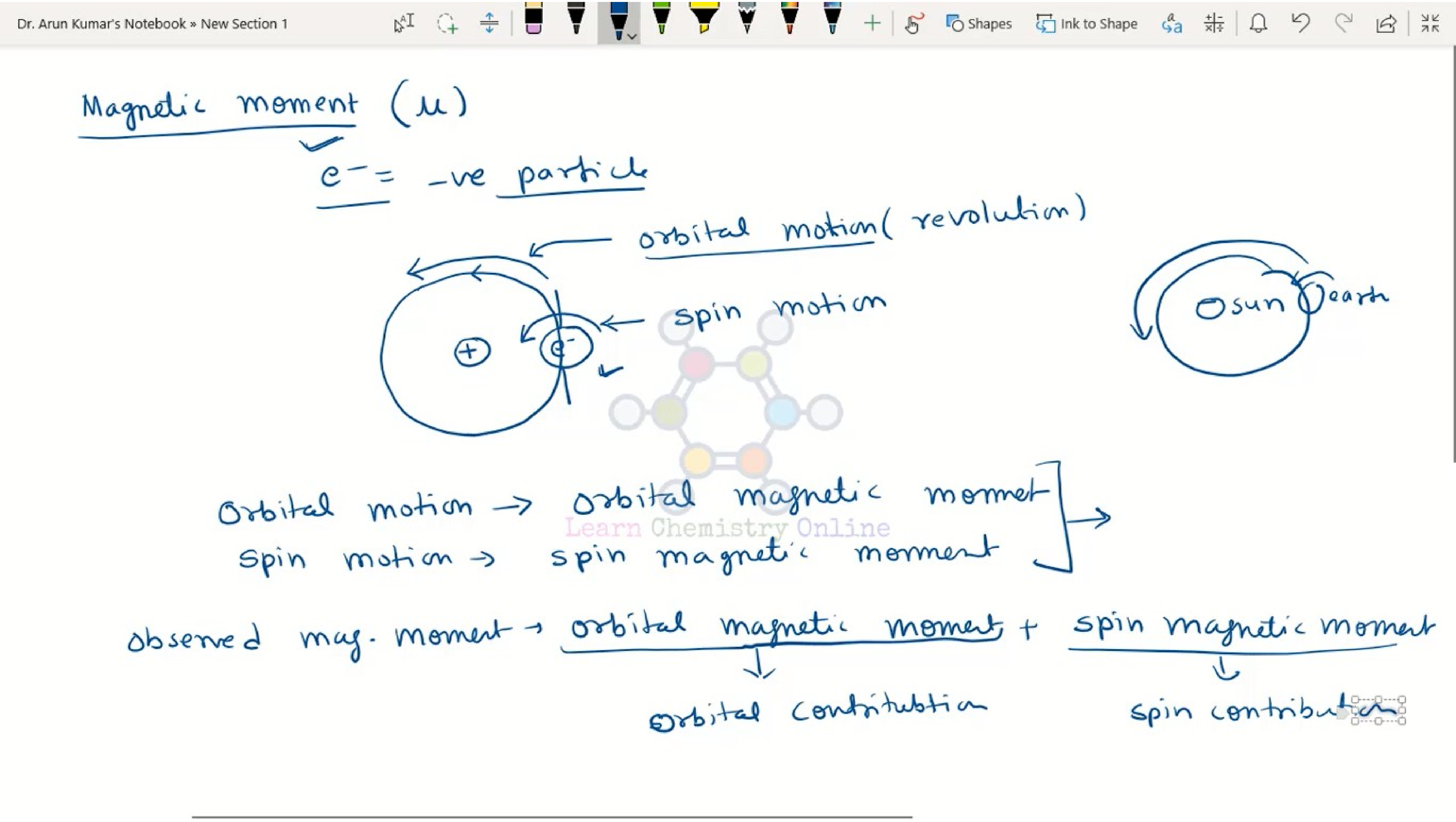
② Diamagnetic

③ Ferromagnetic

① Paramagnetic substance

- Attract → paramagnetic
- unpaired e^-
- Gouy magnetic balance





Magnetic moment (μ)

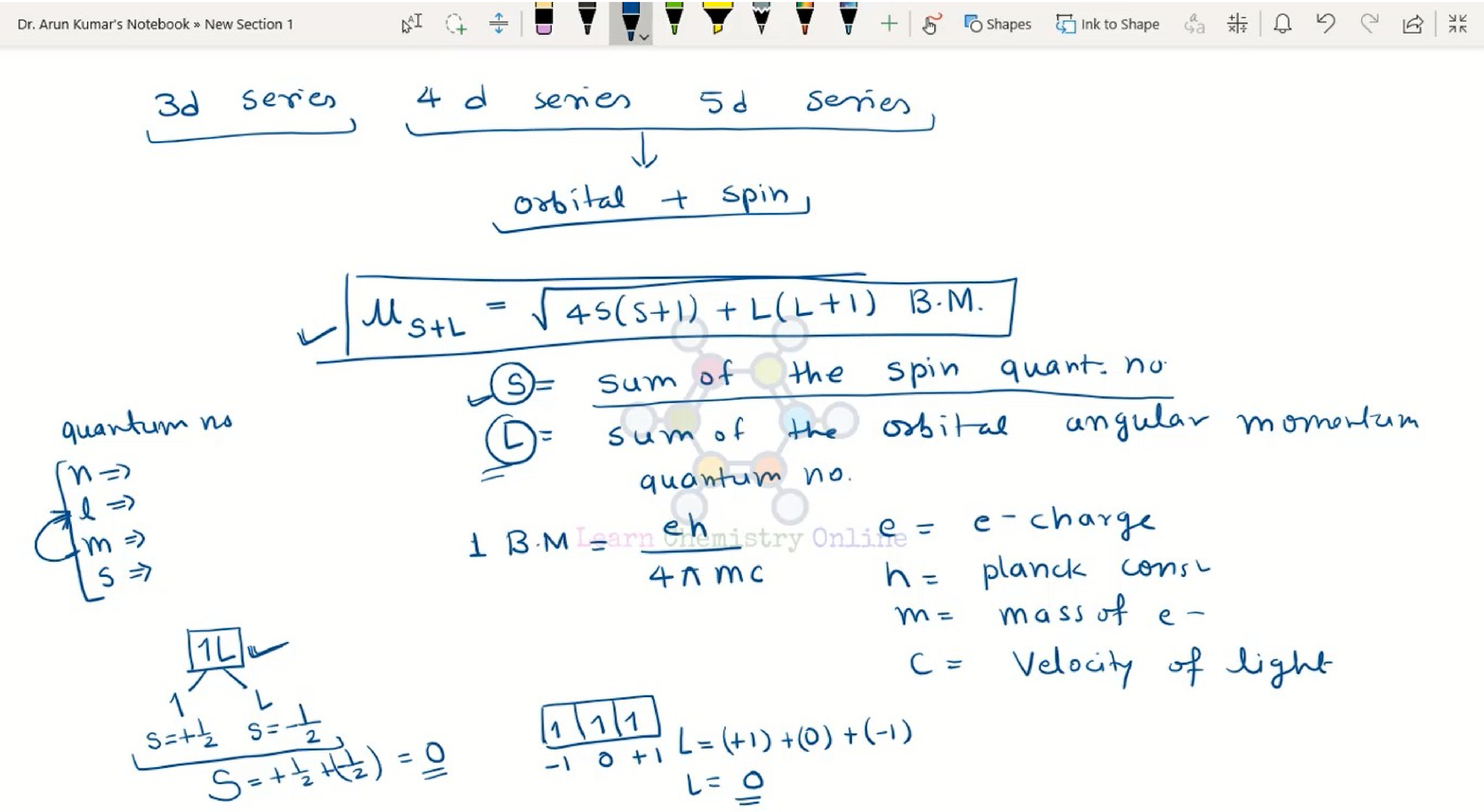
e^- = -ve particle

orbital motion (revolution)

spin motion

Orbital motion → orbital magnetic moment
spin motion → spin magnetic moment

observed mag. moment → $\underbrace{\text{orbital magnetic moment}}_{\text{Orbital contritubtion}}$ + $\underbrace{\text{spin magnetic moment}}_{\text{spin contribution}}$



3d series 4 d series 5d series

↓

orbital + spin

✓ $\boxed{\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}\ \text{B.M.}}$

✓ Ⓢ= sum of the spin quant. no

Ⓛ= sum of the orbital angular momentum quantum no.

$1\ \text{B.M} = \frac{eh}{4\pi mc}$

e = e - charge

h = planck const

m = mass of e -

c = Velocity of light

quantum no

n ⇒

l ⇒

m ⇒

s ⇒

$\boxed{\uparrow\downarrow}$ ✓

$S = +\frac{1}{2}$ $S = -\frac{1}{2}$

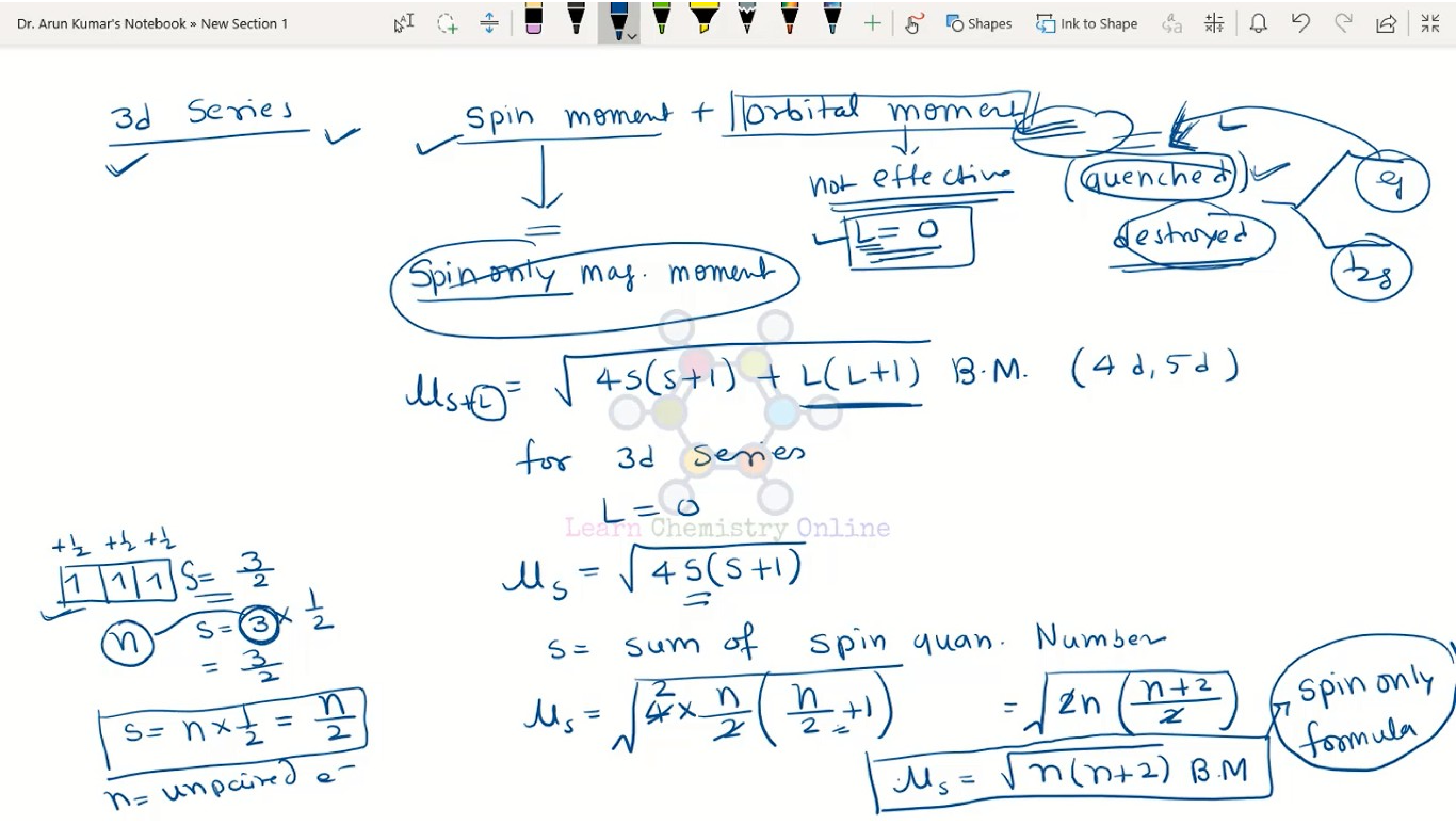
$S = +\frac{1}{2} + (-\frac{1}{2}) = \underline{\underline{0}}$

$\boxed{\uparrow|\uparrow|\uparrow}$

-1 0 +1

$L = (+1) + (0) + (-1)$

$L = \underline{\underline{0}}$



3d Series ✓ ✓

✓ Spin moment + Orbital moment

not effective

✓ $\boxed{L = 0}$

(quenched) ✓

destroyed

Spin only mag. moment

$$\mu_{s+\text{Ⓛ}} = \sqrt{4S(S+1) + L(L+1)}\ \text{B.M.} \quad (4d, 5d)$$

for 3d Series

$L = 0$

$$\mu_s = \sqrt{4S(S+1)}$$

S = sum of spin quan. Number

$$\mu_s = \sqrt{\cancel{4}^{2} \times \frac{n}{\cancel{2}}\left(\frac{n}{2}+1\right)} = \sqrt{\cancel{2}n\left(\frac{n+2}{\cancel{2}}\right)}$$

$$\boxed{\mu_s = \sqrt{n(n+2)}\ \text{B.M}}$$ → spin only formula

$+\frac{1}{2}$ $+\frac{1}{2}$ $+\frac{1}{2}$

| 1 | 1 | 1 | $S = \frac{3}{2}$ ✓

ⓝ $S = ③ \times \frac{1}{2}$

$= \frac{3}{2}$

$$\boxed{S = n \times \frac{1}{2} = \frac{n}{2}}$$

n = unpaired e^-

example ① $\boxed{Fe^{+3}}$

$Fe = \underline{3d^6}\ \underline{4s^2}$ ✓

$Fe^{+3} = \underline{3d^5\ 4s^0}$

↑	↑	↑	↑	↑

$n = 5$

$\mu_s = \sqrt{n(n+2)}$ B.M.

$= \sqrt{5(5+2)}$

$= \sqrt{5(7)}$

$= \sqrt{35}$

$\mu_s = 5.92$ B.M.

② Mn^{+2}

$Mn = 3d^5\ 4s^2$

$Mn^{+2} = \underline{3d^5}\ 4s^0$

$n = 5 \quad \mu_s = 5.92$ B.M.

③ Ni^{+2}

$Ni = 3d^8\ 4s^2$

$Ni^{+2} = 3d^8\ 4s^0$

↑↓	↑↓	↑↓	↑	↑

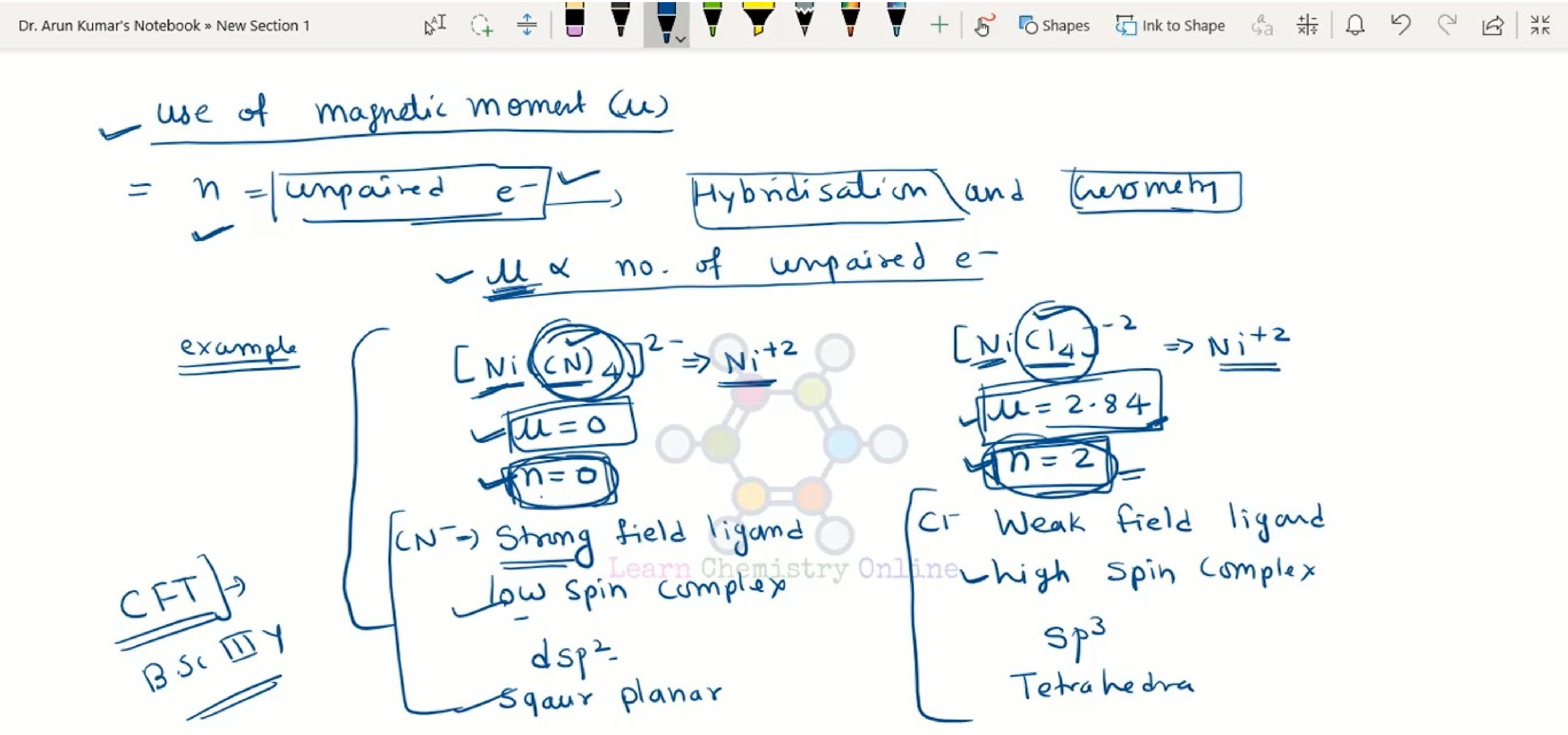
$\boxed{n = 2}$

$\mu_s = \sqrt{n(n+2)}$ B.M.

$= \sqrt{2(2+2)}$

$= \sqrt{2(4)}$

$= \sqrt{8} \quad = \quad 2.84$ B.M



✓ Use of magnetic moment (μ)

= n = $\boxed{\text{unpaired } e^-}$ ✓ → $\boxed{\text{Hybridisation}}$ and $\boxed{\text{Geometry}}$

✓

✓ $\mu \propto$ no. of unpaired e^-

example

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

✓ $\boxed{\mu = 0}$

✓ $\boxed{n = 0}$

$CN^- \rightarrow$ Strong field ligand

✓ low spin complex

dsp^2

Sqaur planar

$[NiCl_4]^{-2} \Rightarrow Ni^{+2}$

✓ $\boxed{\mu = 2.84}$

✓ $\boxed{n = 2}$

Cl^- Weak field ligand

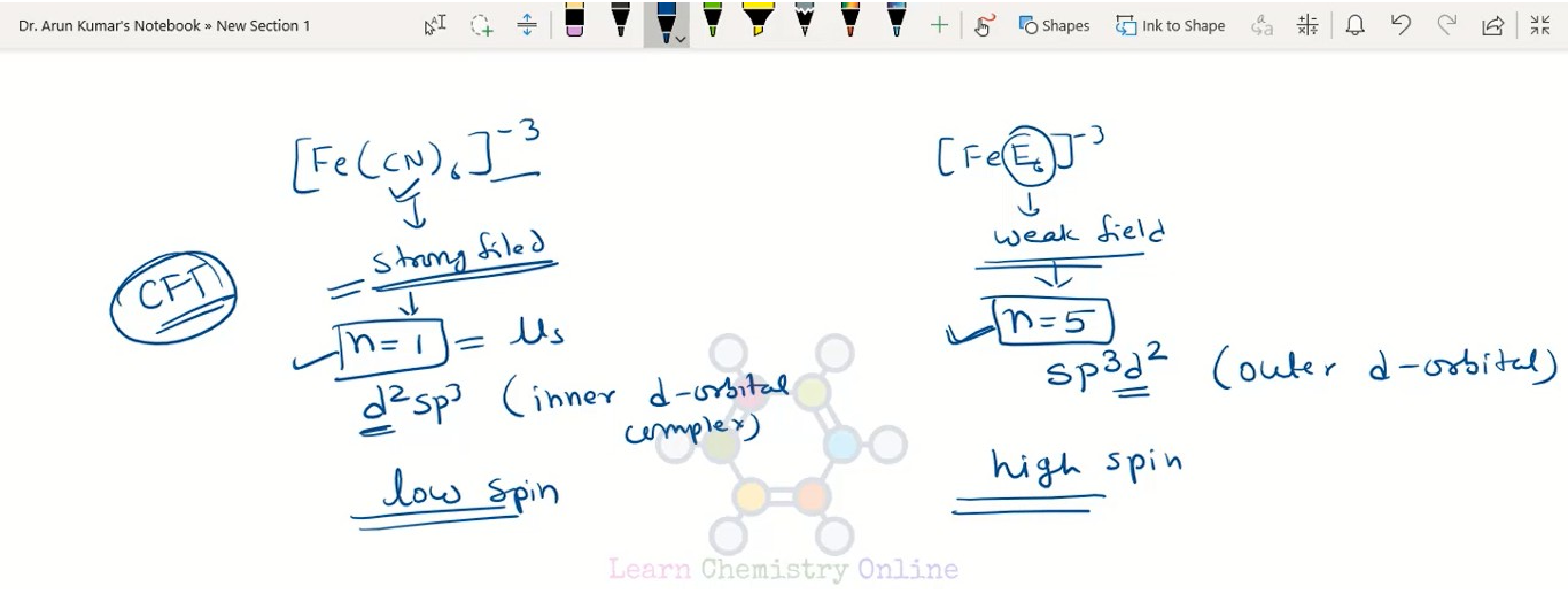
✓ high spin complex

Sp^3

Tetrahedra

$\boxed{\text{CFT}}$ →

B.Sc $\boxed{\text{III}}$ Y



CFT

$[Fe(CN)_6]^{-3}$

$\downarrow$

strong filed

$\downarrow$

$\boxed{n = 1} = \mu_s$

d^2sp^3 (inner d-orbital complex)

low spin

$[FeE_6]^{-3}$

$\downarrow$

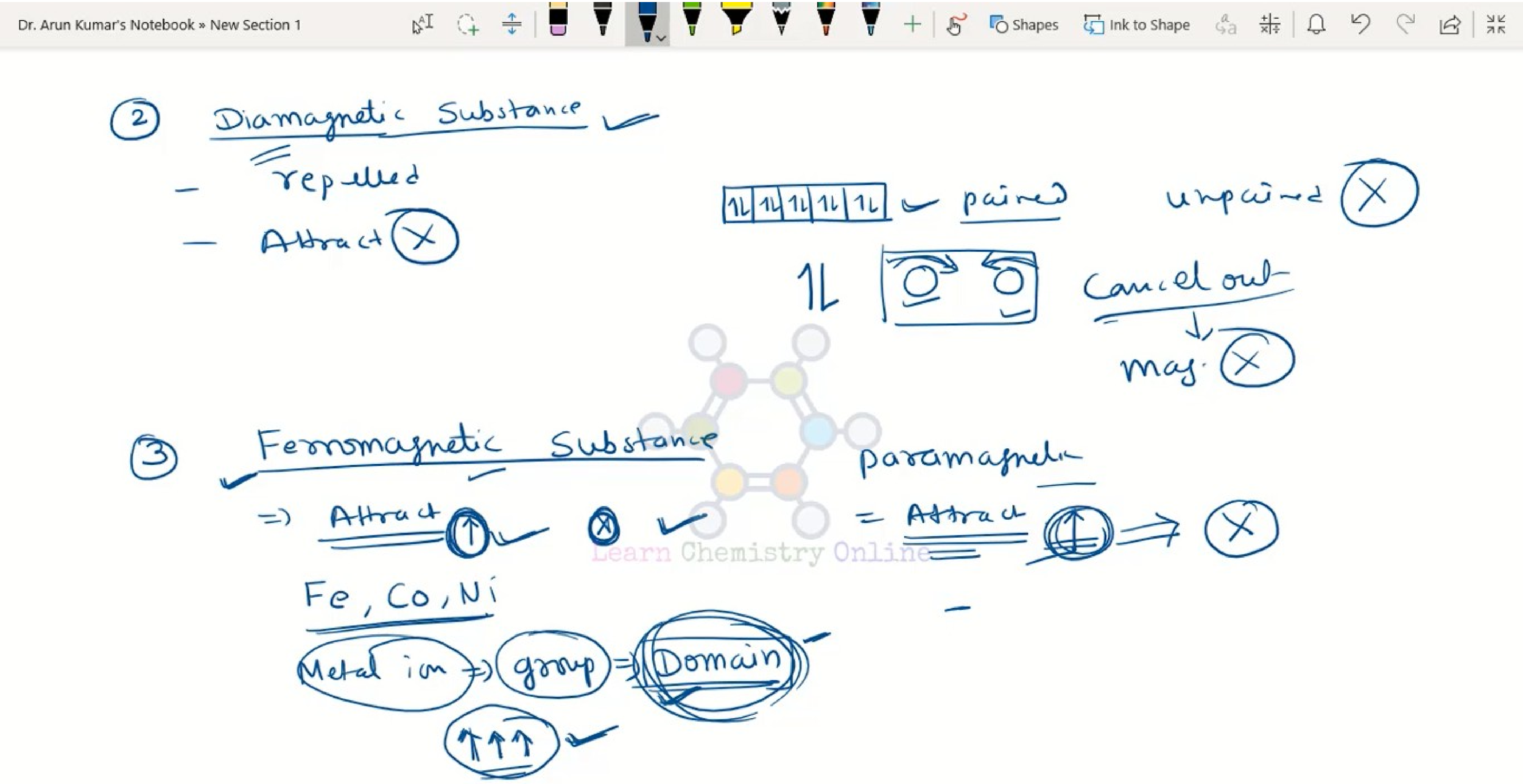
weak field

$\downarrow$

$\boxed{n = 5}$

sp^3d^2 (outer d-orbital)

high spin



② Diamagnetic Substance ✓

- repelled
- Attract Ⓧ

1L 1L 1L 1L 1L ✓ paired   unpaired Ⓧ

$\uparrow\downarrow$ Cancel out ↓ mag. Ⓧ

③ Ferromagnetic Substance ✓

⇒ Attract ⓘ ✓   Ⓧ ✓

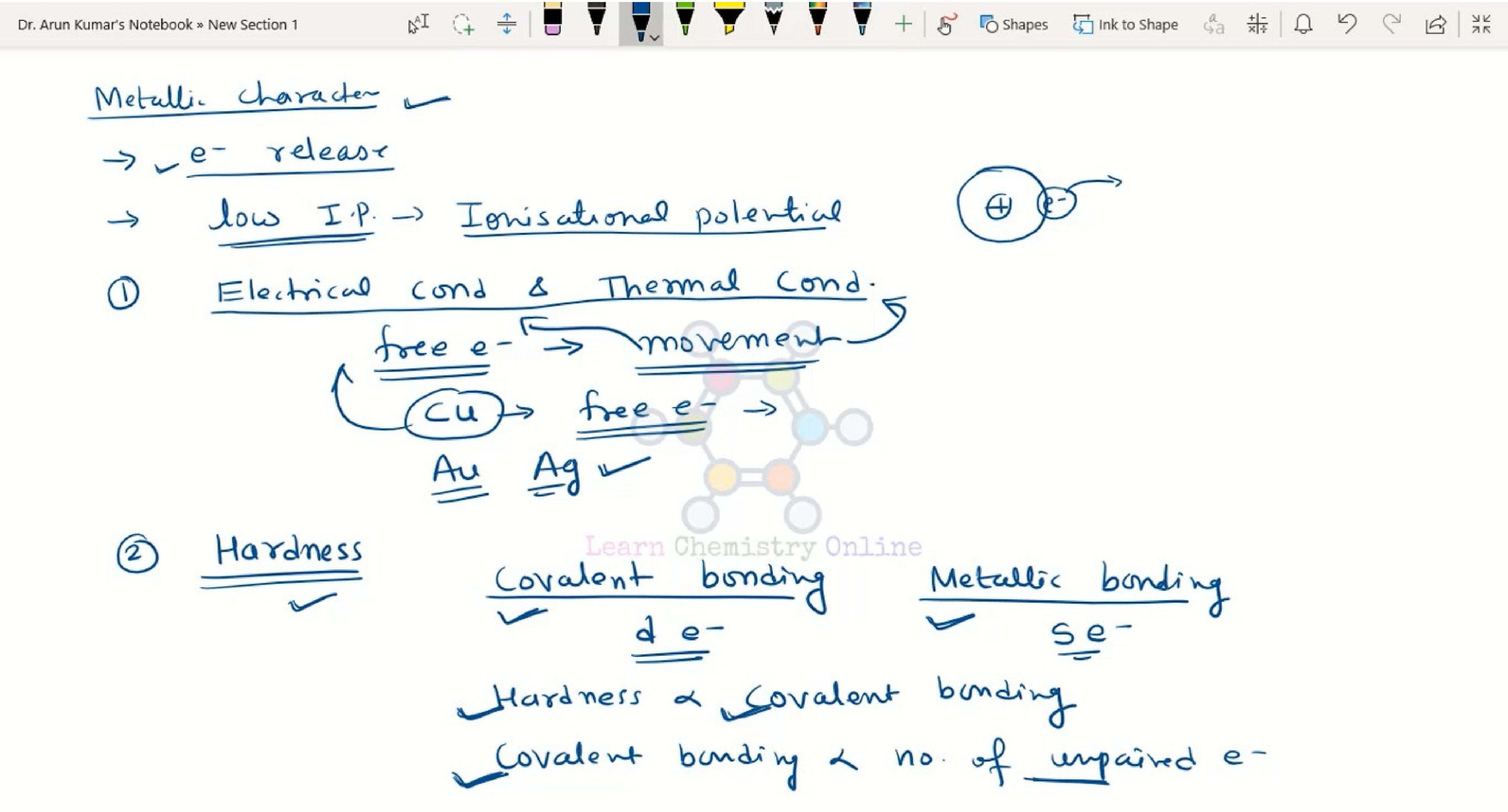
Fe, Co, Ni

Metal ion ⇒ group ⇒ Domain ✓

↑↑↑ ✓

paramagnetic

= Attract $\updownarrow$ ⇒ Ⓧ



Metallic character ✓

→ ✓ e^- release

→ low I.P. → Ionisational potential

① Electrical cond & Thermal cond.

free e^- → movement

Cu → free e^- →

Au Ag ✓

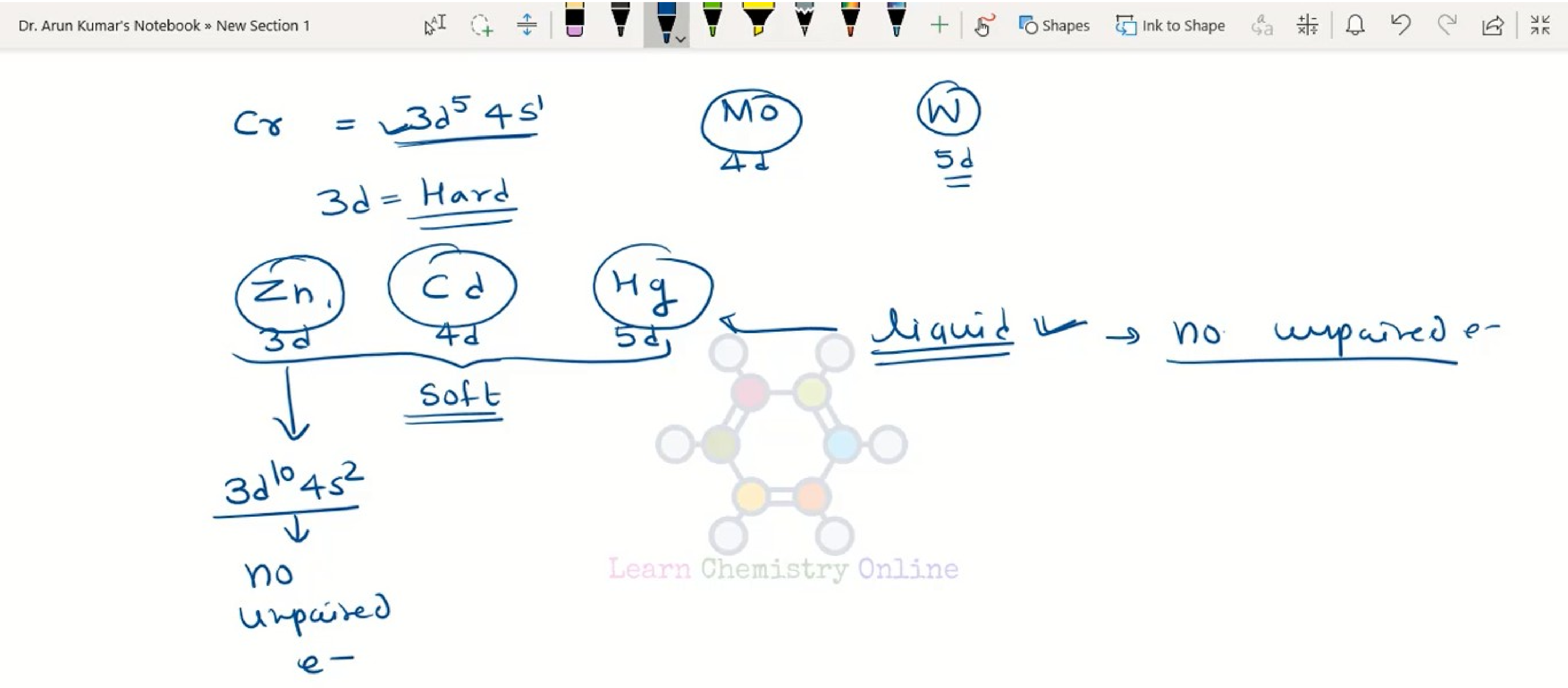
② Hardness ✓

Covalent bonding ✓ | Metallic bonding ✓

d e^- | s e^-

✓ Hardness $\propto$ ✓ Covalent bonding

✓ Covalent bonding $\propto$ no. of unpaired e^-



Cr = $3d^5 4s^1$

3d = Hard

Mo
4d

W
5d

Zn
3d

Cd
4d

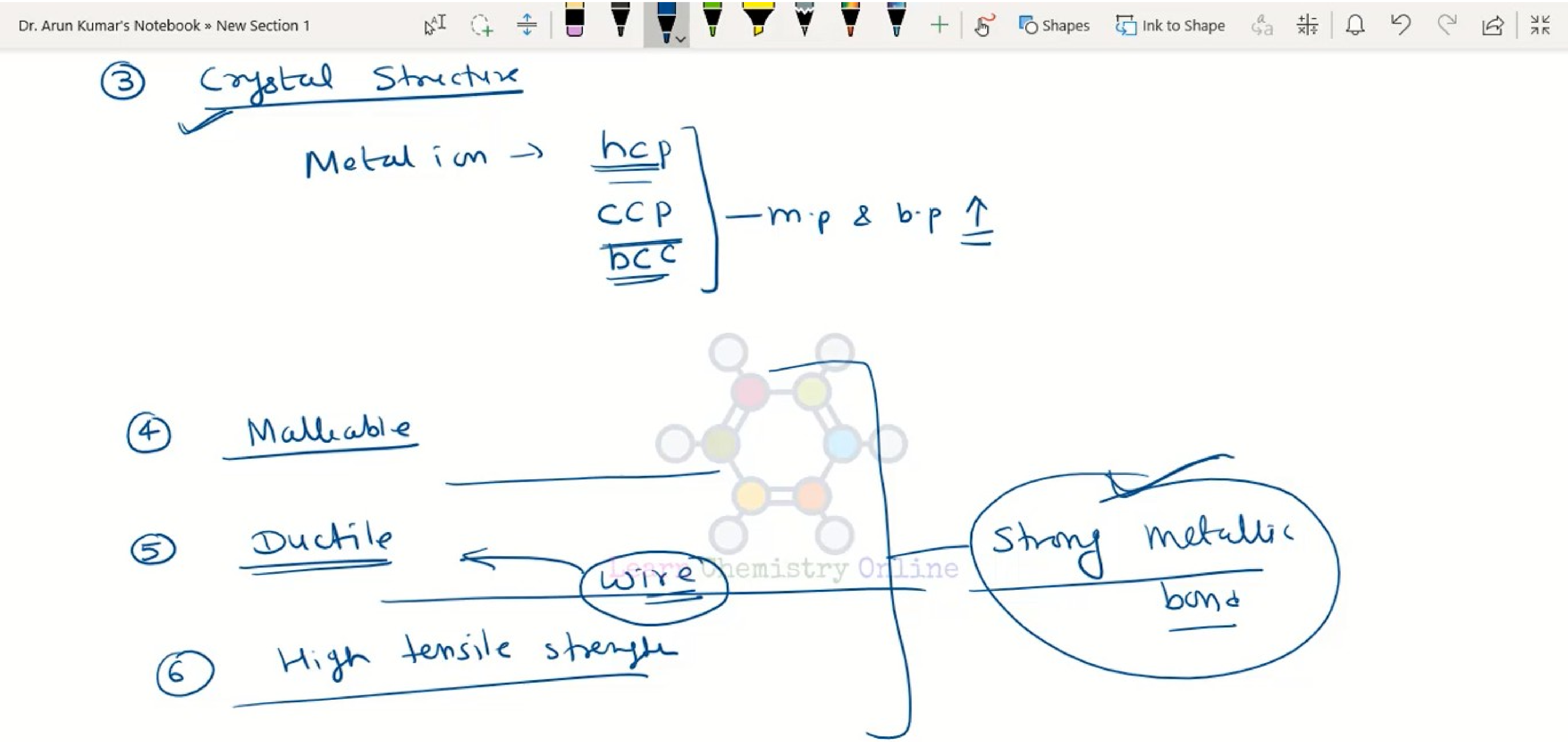
Hg
5d

Soft

$3d^{10} 4s^2$
↓
no unpaired e^-

liquid ← Hg

liquid → no unpaired e^-



③ **Crystal Structure**

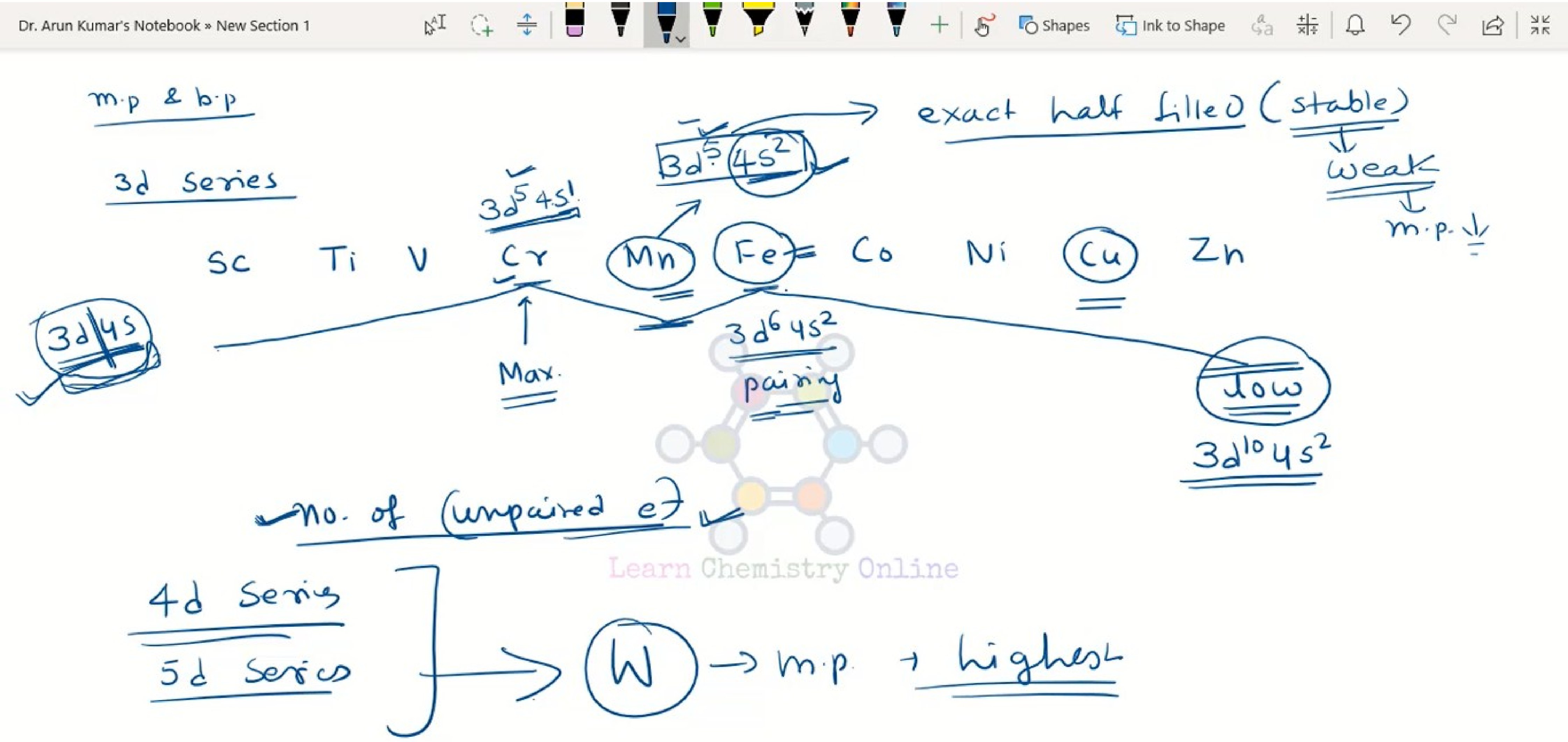
Metal ion → hcp / ccp / bcc } — m.p & b.p ↑

④ Malleable

⑤ Ductile ← Wire

⑥ High tensile strength

} — Strong metallic bond



m.p & b.p

3d series

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Cr: $3d^5 4s^1$

Max.

Mn → $3d^5 4s^2$ → exact half filled (stable) ↓ weak ↓ m.p. ↓

Fe: $3d^6 4s^2$

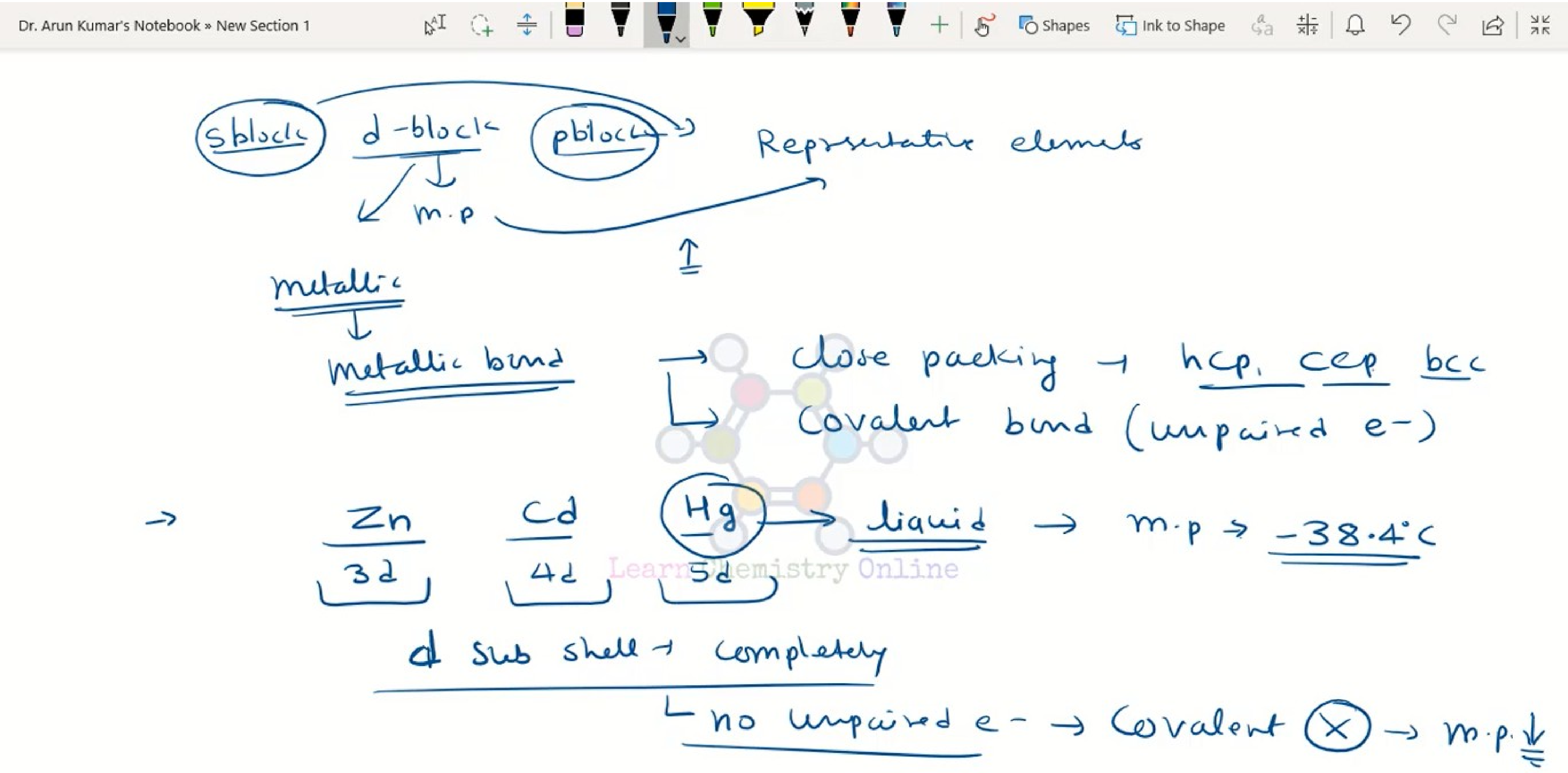
pairing

Zn: low, $3d^{10} 4s^2$

3d | 4s

no. of (unpaired e^-)

4d series
5d series → W → m.p. → highest



s block d-block p block → Representative elements

d-block ↓ m.p ↑

metallic

↓

metallic bond → close packing → hcp, ccp bcc

↳ Covalent bond (unpaired e−)

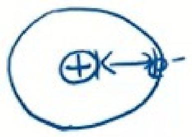
→ Zn Cd Hg → liquid → m.p → −38.4°C

3d 4d 5d

d sub shell → completely

└ no unpaired e− → Covalent ⊗ → m.p. ↓

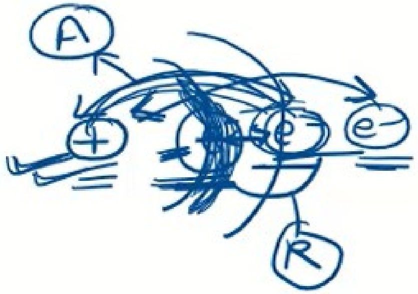
Atomic Radius & Ionic Radius



Factors

① Nucleus Charge $\propto \frac{1}{size}$

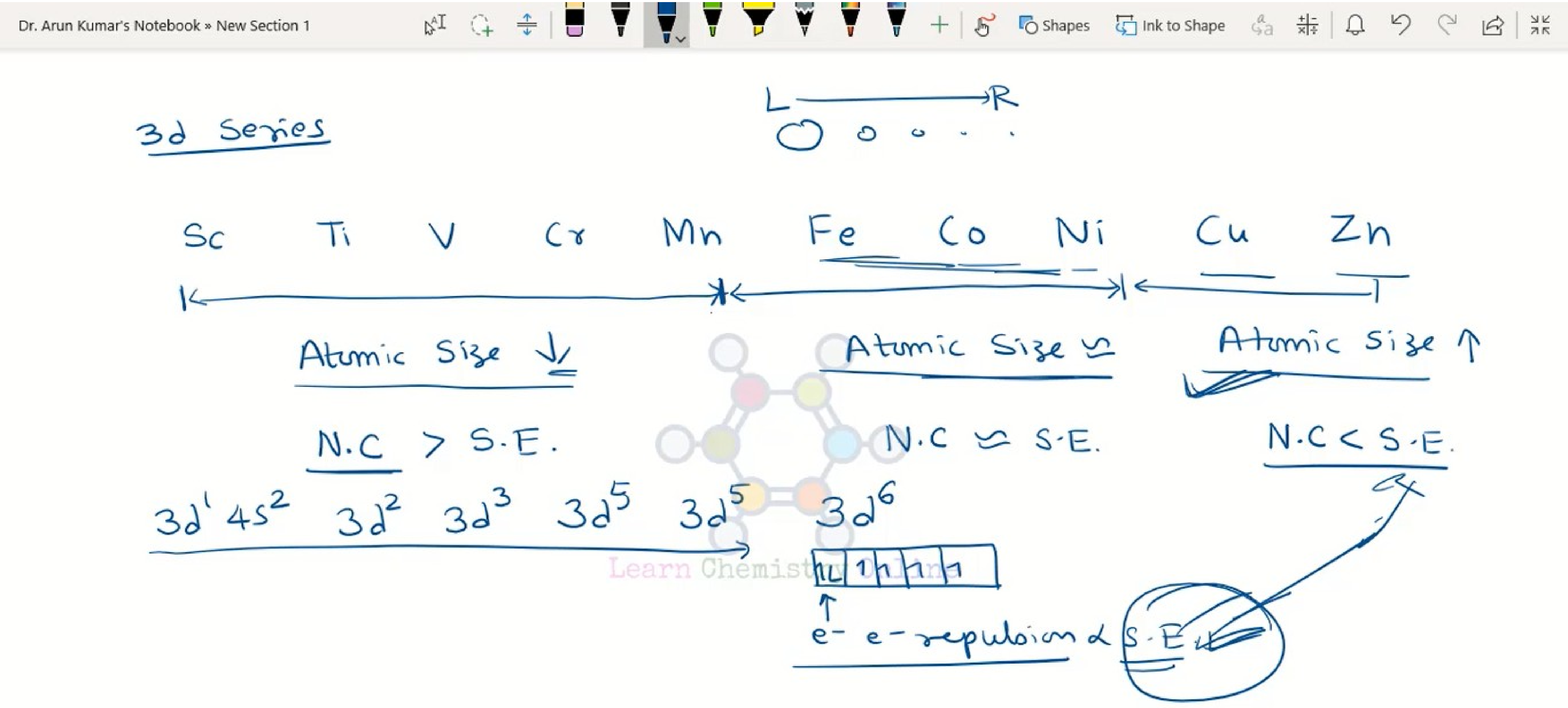
② Shielding effect $\propto$ size



③ Effective Nuclear charge

$Z_{eff} \rightarrow N.C - \boxed{S.E}$

⑧ = 10 − 2



3d Series

$L \longrightarrow R$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1 4s^2$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$				

Sc → Mn: Atomic Size ↓

$N.C > S.E.$

Mn → Ni: Atomic Size ≃

$N.C \simeq S.E.$

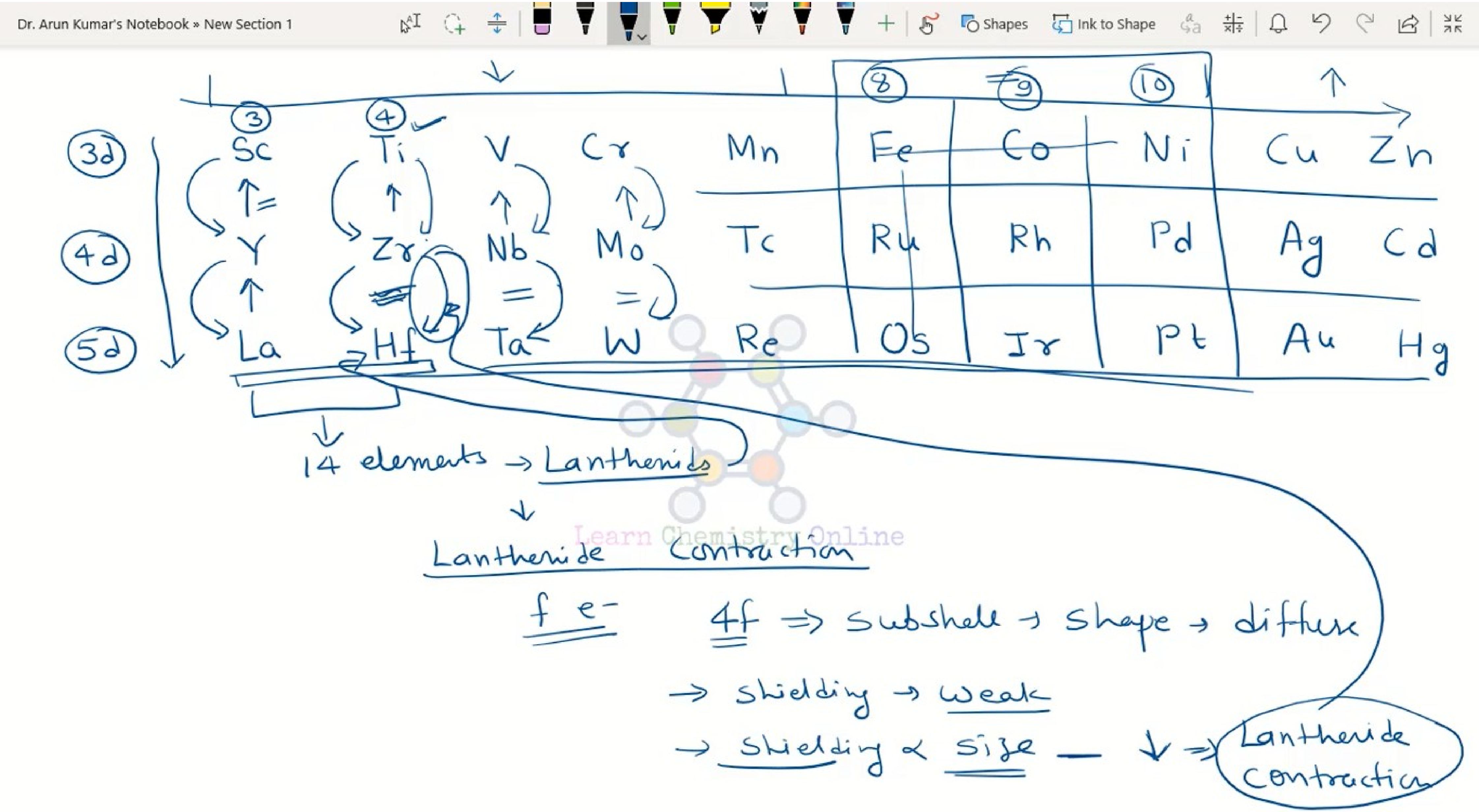
Ni → Zn: Atomic Size ↑

$N.C < S.E.$

$3d^6$: $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

↑

e^- e^- repulsion $\propto$ $\boxed{S.E.\uparrow}$



Dr. Arun Kumar's Notebook » New Section 1

	③	④				⑧	⑨	⑩		
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	↑=	↑	↑	↑						
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	↑	=	=	=						
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

14 elements → Lanthenids

↓

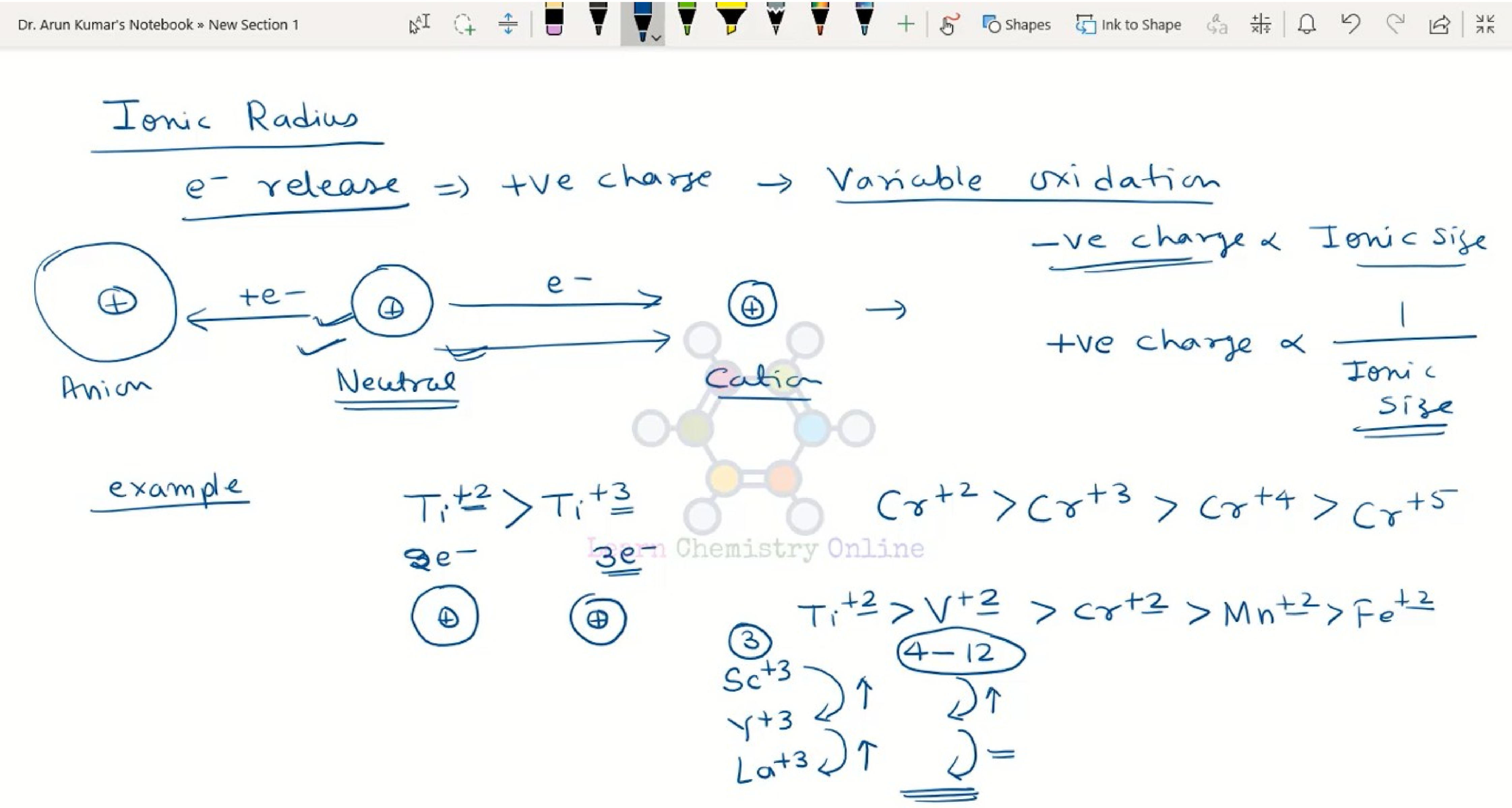
Lanthenide Contraction

f e-

4f ⇒ subshell → shape → diffuse

→ shielding → weak

→ shielding ∝ size — ↓ ⇒ Lanthenide Contraction



Ionic Radius

e^- release ⇒ +ve charge → Variable oxidation

$-ve$ charge ∝ Ionic size

+ve charge ∝ $\frac{1}{\text{Ionic size}}$

example

$Ti^{+2} > Ti^{+3}$

$2e^-$ $3e^-$

$Cr^{+2} > Cr^{+3} > Cr^{+4} > Cr^{+5}$

$Ti^{+2} > V^{+2} > Cr^{+2} > Mn^{+2} > Fe^{+2}$

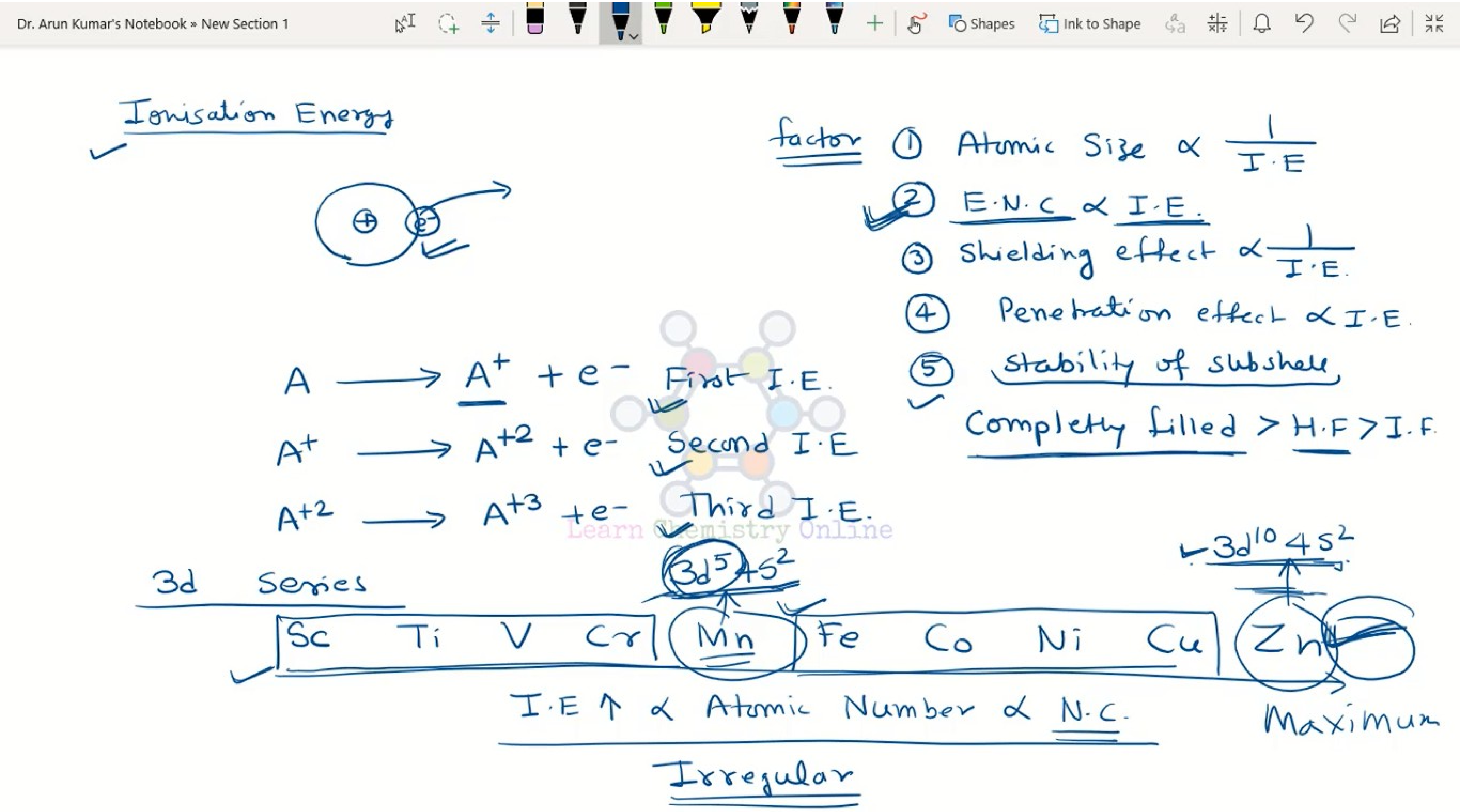
$\boxed{4-12}$ ↑ ↑ =

③

Sc^{+3} ↑

Y^{+3} ↑

La^{+3}



Ionisation Energy ✓

$$A \longrightarrow \underline{A^{+}} + e^{-}$$ First I.E. ✓

$$A^{+} \longrightarrow A^{+2} + e^{-}$$ Second I.E ✓

$$A^{+2} \longrightarrow A^{+3} + e^{-}$$ Third I.E. ✓

factor

① Atomic Size $\propto \frac{1}{I.E}$

✓ ② E.N.C $\propto$ I.E.

③ Shielding effect $\propto \frac{1}{I.E.}$

④ Penetration effect $\propto$ I.E.

⑤ Stability of subshell ✓

Completely filled > H.F > I.F.

3d Series ✓

Sc Ti V Cr Mn Fe Co Ni Cu Zn

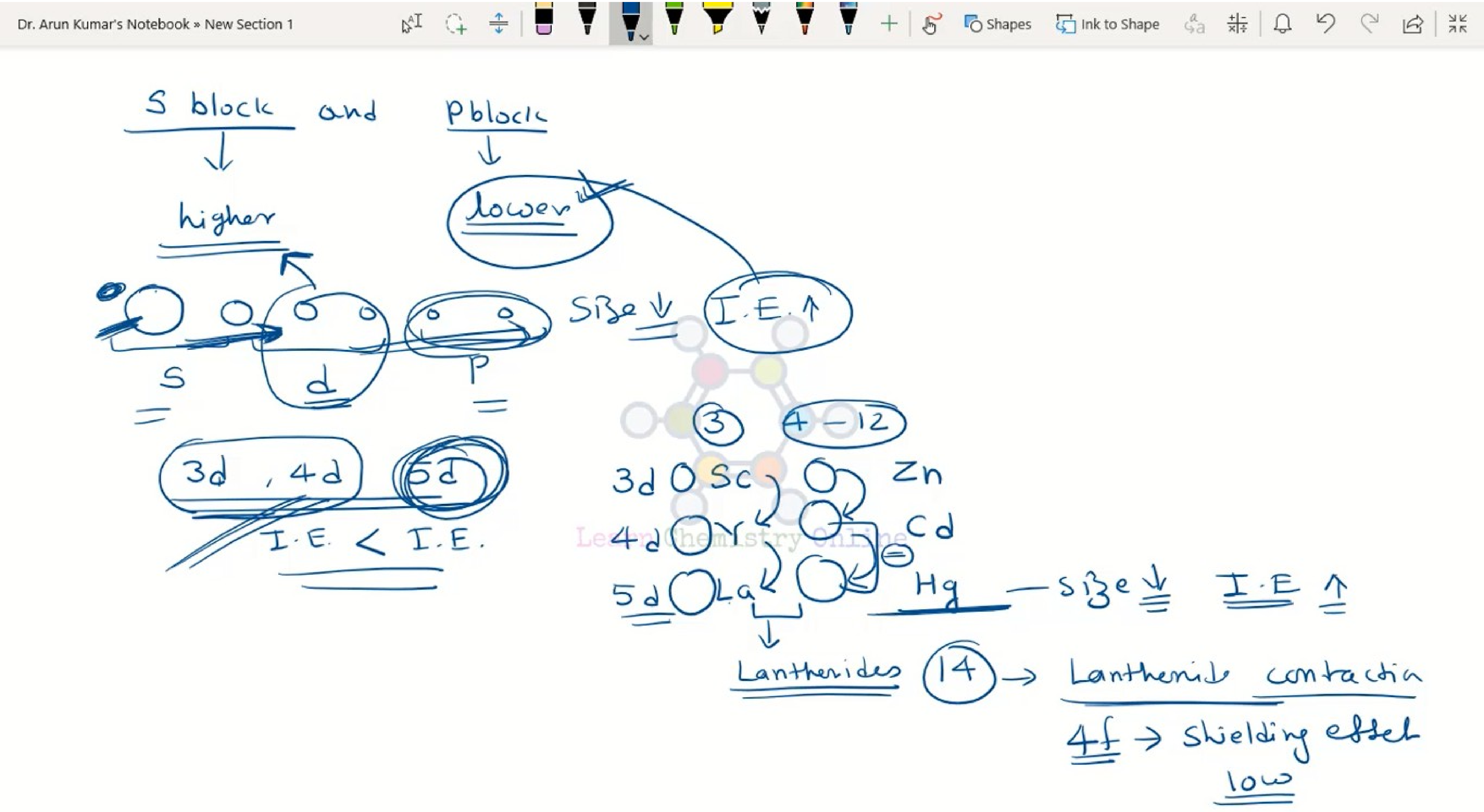
$3d^5 4s^2$ (Mn)

$3d^{10} 4s^2$ (Zn) ✓

Maximum

I.E ↑ $\propto$ Atomic Number $\propto$ N.C.

Irregular



S block and p block

↓ ↓

higher lower

S d p

Size ↓ I.E. ↑

3d , 4d 5d

I.E. < I.E.

③ 4 – 12

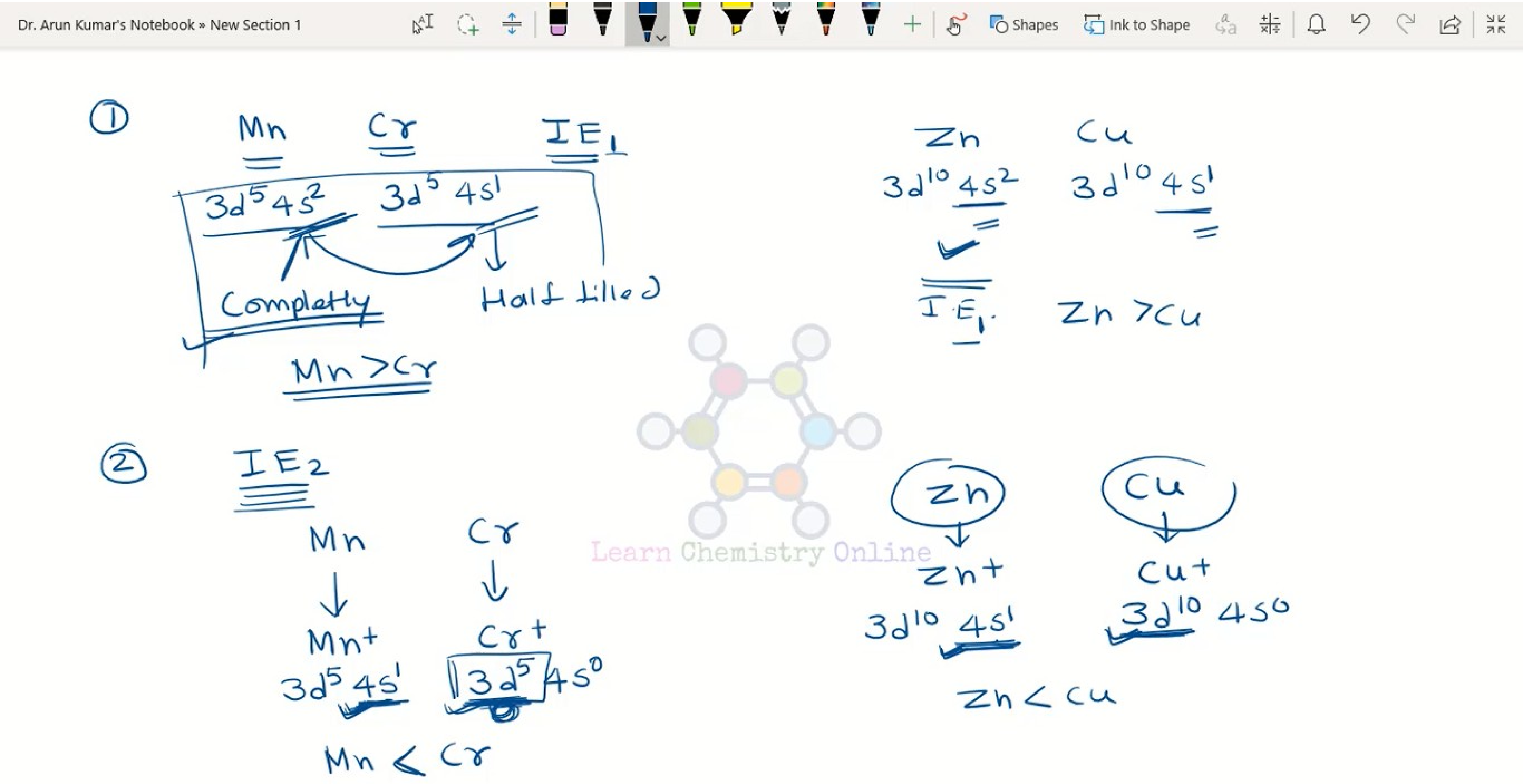
3d Sc Zn

4d Y Cd

5d La Hg — size ↓ I.E ↑

Lanthenides ⑭ → Lanthenide contractin

4f → shielding effect low



① Mn Cr IE_1

$3d^5 4s^2$ $3d^5 4s^1$

Completly Half filled

Mn > Cr

② IE_2

Mn → Mn^+ $3d^5 4s^1$

Cr → Cr^+ $\boxed{3d^5}$ $4s^0$

Mn < Cr

Zn Cu

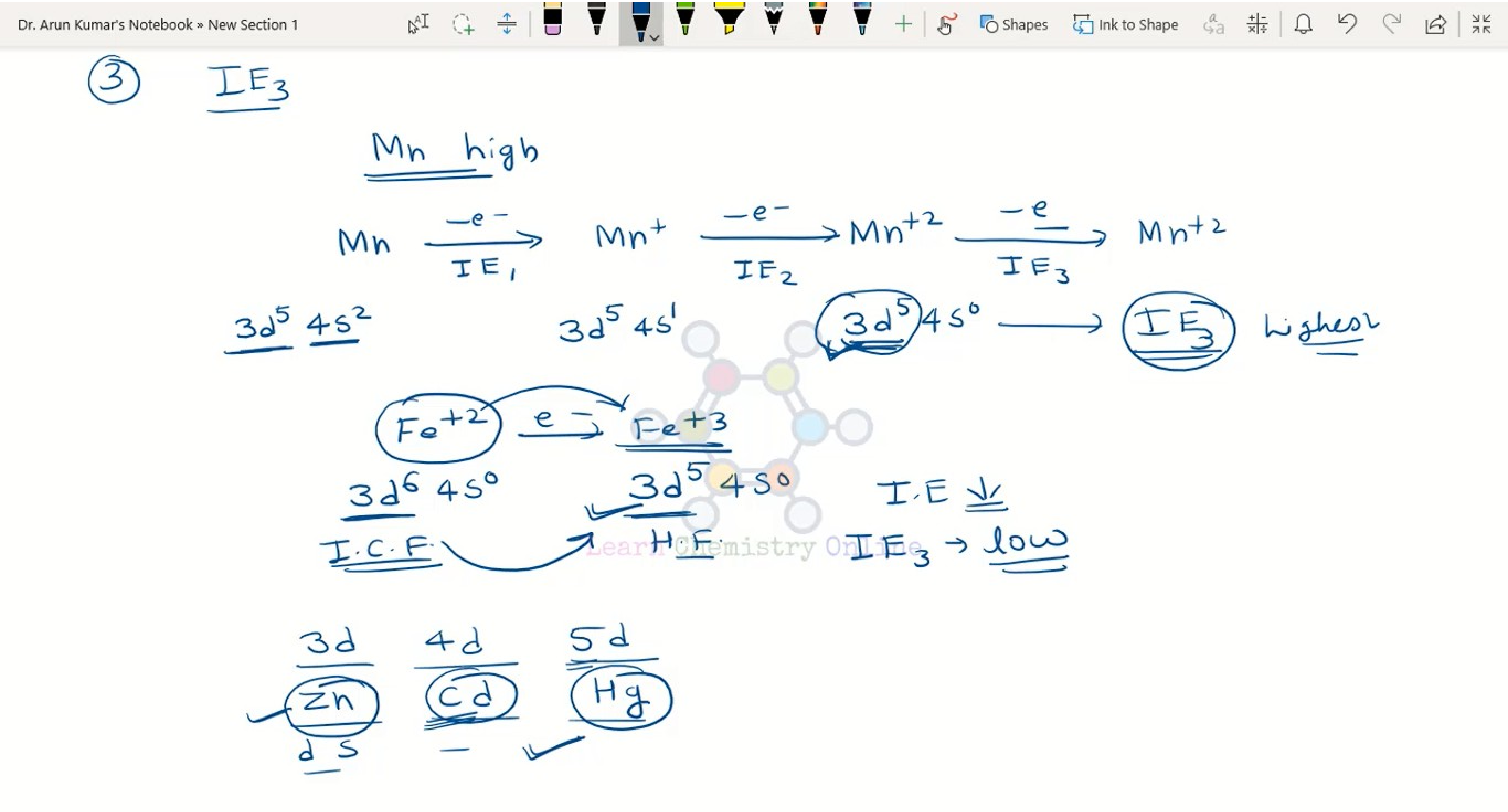
$3d^{10} 4s^2$ ✓ $3d^{10} 4s^1$

IE_1. Zn > Cu

Zn → Zn^+ $3d^{10} 4s^1$

Cu → Cu^+ $3d^{10} 4s^0$

Zn < Cu



③ IE_3

Mn high

$$Mn \xrightarrow[IE_1]{-e^-} Mn^+ \xrightarrow[IE_2]{-e^-} Mn^{+2} \xrightarrow[IE_3]{-e} Mn^{+2}$$

$3d^5\ 4s^2$ $3d^5\ 4s^1$ $3d^5\ 4s^0 \longrightarrow IE_3$ highest

$Fe^{+2} \xrightarrow{e^-} Fe^{+3}$

$3d^6\ 4s^0$ ✓ $3d^5\ 4s^0$ I.E ↓

I.C.F → H.F $IE_3 \to$ low

3d	4d	5d
✓ Zn	Cd	Hg
d s	—	✓

Zn, Cu, Ni → $\underline{(+2)}$ → highly stable

Zn

$3d^{10}\underline{4s^2}$

$\underline{3d^{10}4s^0}$

$\boxed{+2}$

$\cancel{+3}$

$Cu^{+1} \Rightarrow 3d^{10}4s^0$

$Cu^{+2} \Rightarrow 3d^9 4s^0$

$\underline{Ni^{+2}} = \underline{\boxed{3d^8}4s^0}$

$Ni^{+3} \Rightarrow$ less stable $\underline{IE_3} \uparrow$ high

Cu V/s Alkali metals

IE_1 Cu > Alkali metal

$\boxed{3d^{10}}\,4s^1$

↓

diffuse shape

↓

low shielding

↓

Size ↓

I.E. ↑

$\boxed{\text{Noble gas}}\,ns^1$

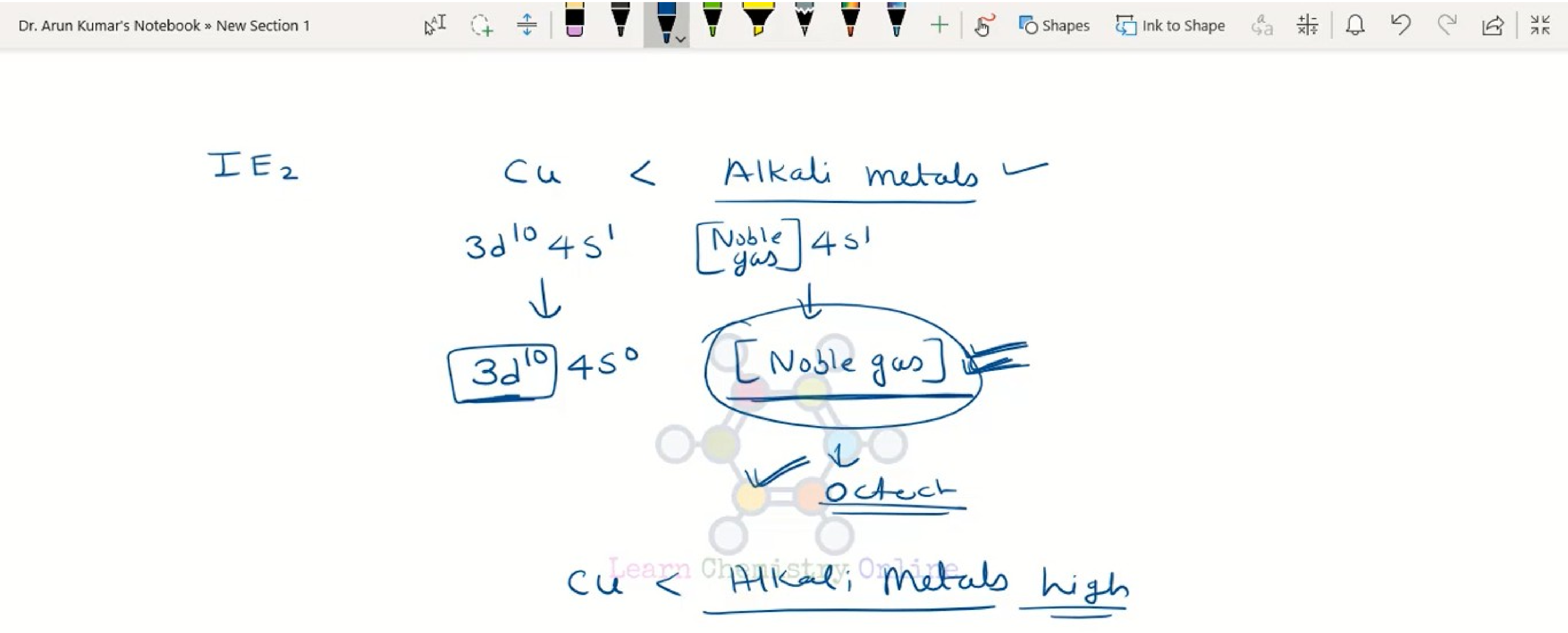
high shielding effect

↓

Size ↑

↓

$I.E._1$ ↓



IE$_2$

Cu < Alkali metals ✓

$3d^{10}4s^1$ [Noble gas] $4s^1$

↓ ↓

$\boxed{3d^{10}}4s^0$ [Noble gas]

↓

Octect

Cu < Alkali Metals high

Catalytic properties and Complex formation

→ unpaired d - e⁻ (Incomplete d-orbital)

→ energy absorb and re-emit (This makes the required energy of activation)

→ Intermiediate comp formation theory $C + R \to \text{Intermediate} \downarrow C + \text{product}$

→ Adsorption theory $\bigcirc^{R} \to \text{surface} \downarrow \text{product}$

example

① **Nickel** → Reduction of unsaturated hydrocarbons (Ethene → Ethane)
↳ Hydrogenation of oil (Vegetable ghee)

② **Pt** → many reaction → Alcohol → Aldehyde

③ Platinised asbestos + V_2O_5 → Contact process (H_2SO_4 formation)

④ Pt → Ostwald's process (HNO_3 formation)

⑤ **Fe** + Mo → Haber process (NH_3 formation)
└ promotor

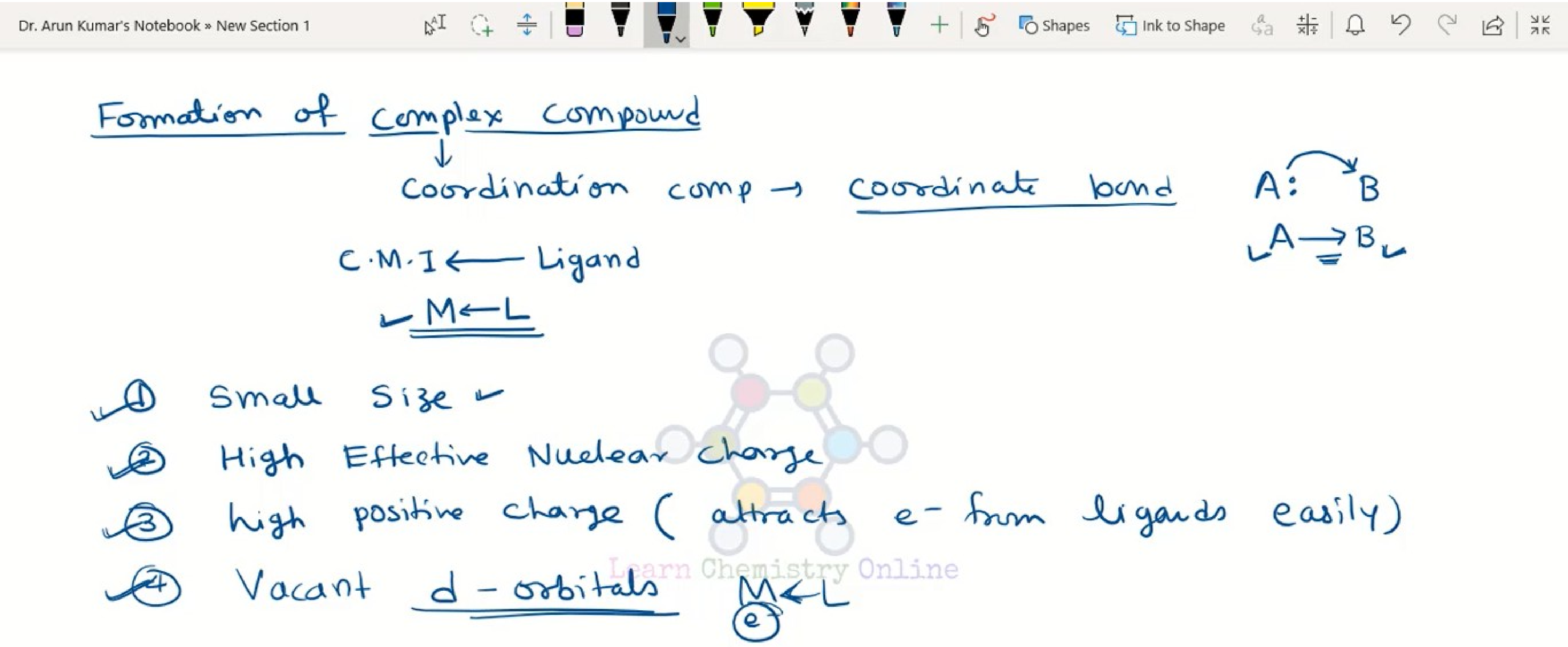
⑥ Fenton Reagent ($FeSO_4 + H_2O_2$) → Alcohol → Aldehyde

⑦ Pd → hydrogenation of phenol

⑧ Ziegler - Natta Catalyst → polyethene └ $TiCl_4 + (C_2H_5)_3Al$

⑨ NiO → manf. of sulphur from coal gas

⑩ Cobalt → Synthesis of petrol (gasoline) → Fischer - Tropsch process



Formation of complex compound

$\downarrow$

Coordination comp → coordinate bond

$A: \curvearrowright B$

✓ $A \rightarrow B$ ✓

C.M.I ⟵ Ligand

✓ $M \leftarrow L$

✓ ① Small Size ✓

✓ ② High Effective Nuclear charge

✓ ③ high positive charge (attracts e- from ligands easily)

✓ ④ Vacant d - orbitals $\underset{e}{M} \leftarrow L$

Stability of complex

$$\left[\text{Stability of complex} \propto \frac{1}{\text{Atomic no.} \checkmark \text{ of } \underline{\text{T.M.}}}\right.$$

- Variable state

higher O.S.	lower O.S.] → $\underline{0}$, $\underline{+1}$
✓ F⁻ Cl⁻ NH_3 etc	↳ $\boxed{\pi\text{-acid ligand}}$ — $M \leftrightarrows L$ ✓ back bonding
	complex CO, NO, CN^- etc

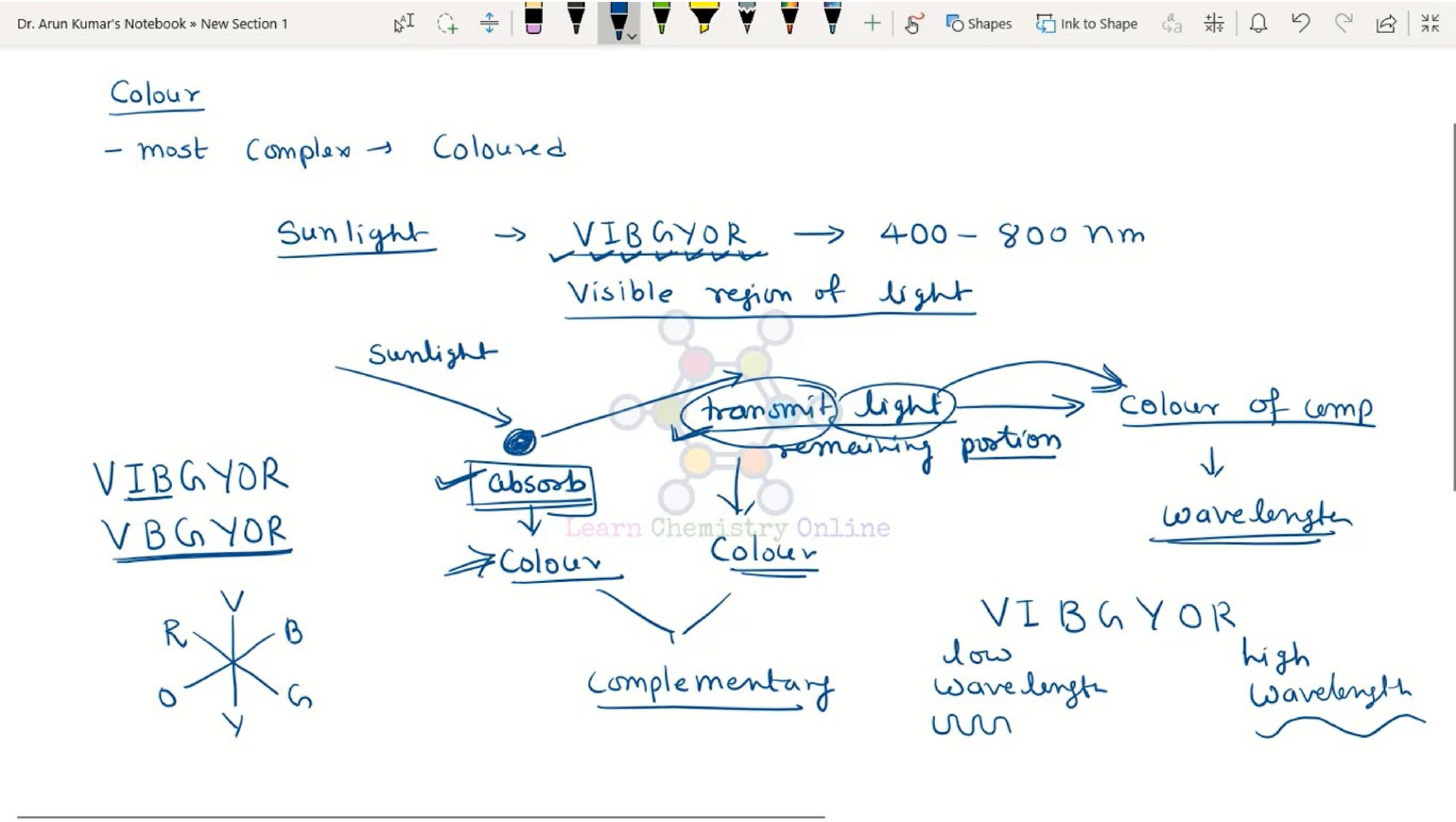
e.g. $Ni(CO)_4 = 0$

$Fe(CO)_5 = 0$

✓ $[Co(NH_3)_6]^{3+} > [Co(NH_3)_6]^{2+}$

- $Co^{+3} \rightarrow$ Small size
- high +ve charge
- easily accepts e⁻ from ligand

- Co^{+2} -



Colour

- most Complex → Coloured

Sunlight → VIBGYOR → 400 - 800 nm

Visible region of light

Sunlight

absorb

Colour

transmit light

remaining portion

Colour

Colour of comp

wavelength

complementary

VIBGYOR

VBGYOR

V B G Y O R

VIBGYOR

low wavelength

high wavelength

$[Co(H_2O)_6]^{2+}$ → Blue green → Red

absorb — transmitted light

aq. sol. $[Ti(H_2O)_6]^{3+}$ → Gree light → purple

Factors on which colour depends

① Nature of metal ion

$[Ti(H_2O)_6]^{+3}$ — purple

$[Co(H_2O)_6]^{3+}$ — Red

② Nature of ligand

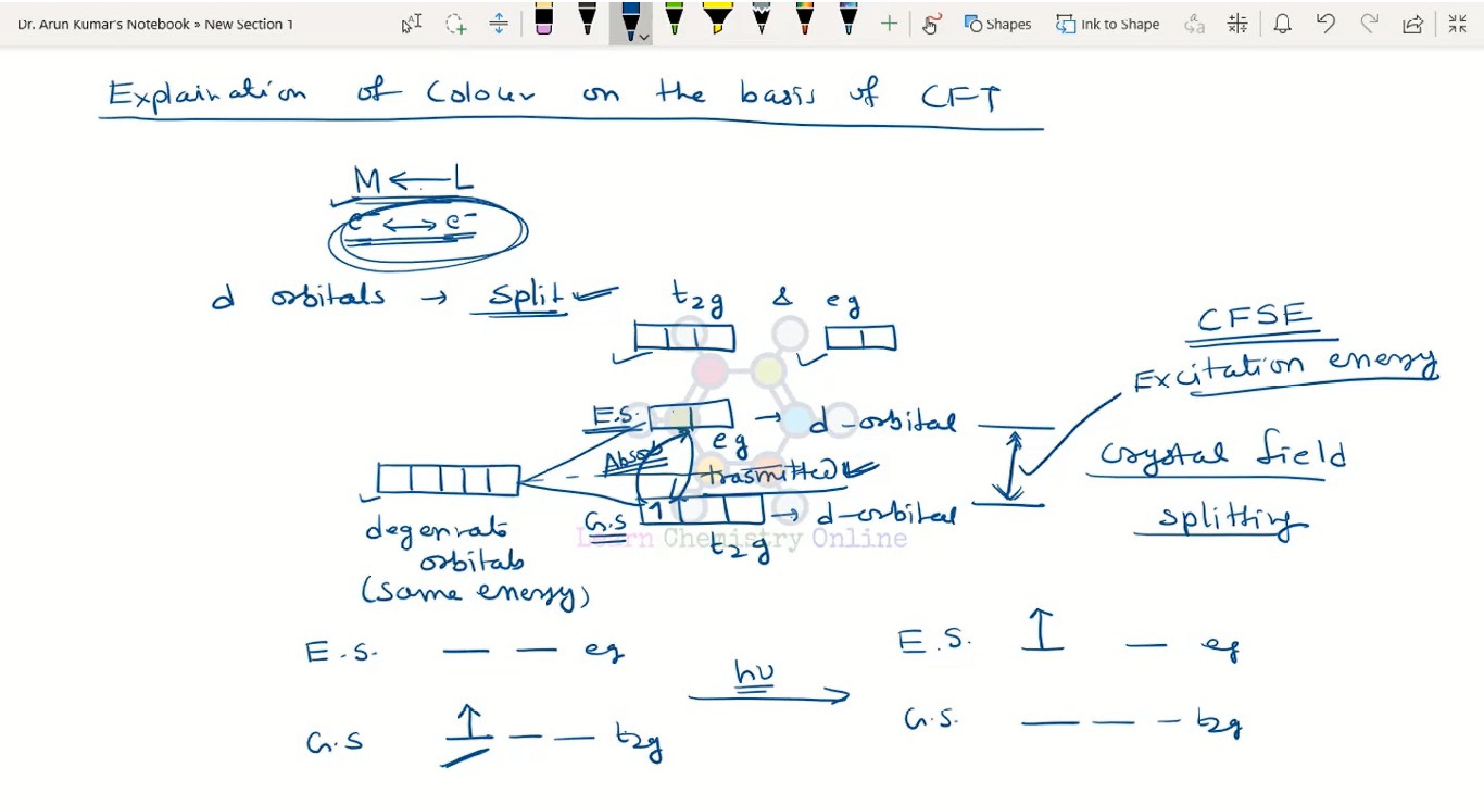
$[Ni(H_2O)_6]^{2+}$ — Blue green

$[Ni(NH_3)_6]^{2+}$ — Blue

Weak ligand — strong ligand

→ spectrochemical Series

CFT



Explaination of Colour on the basis of CFT

M ← L

$e^- \longleftrightarrow e^-$

d orbitals → split t_{2g} & e_g

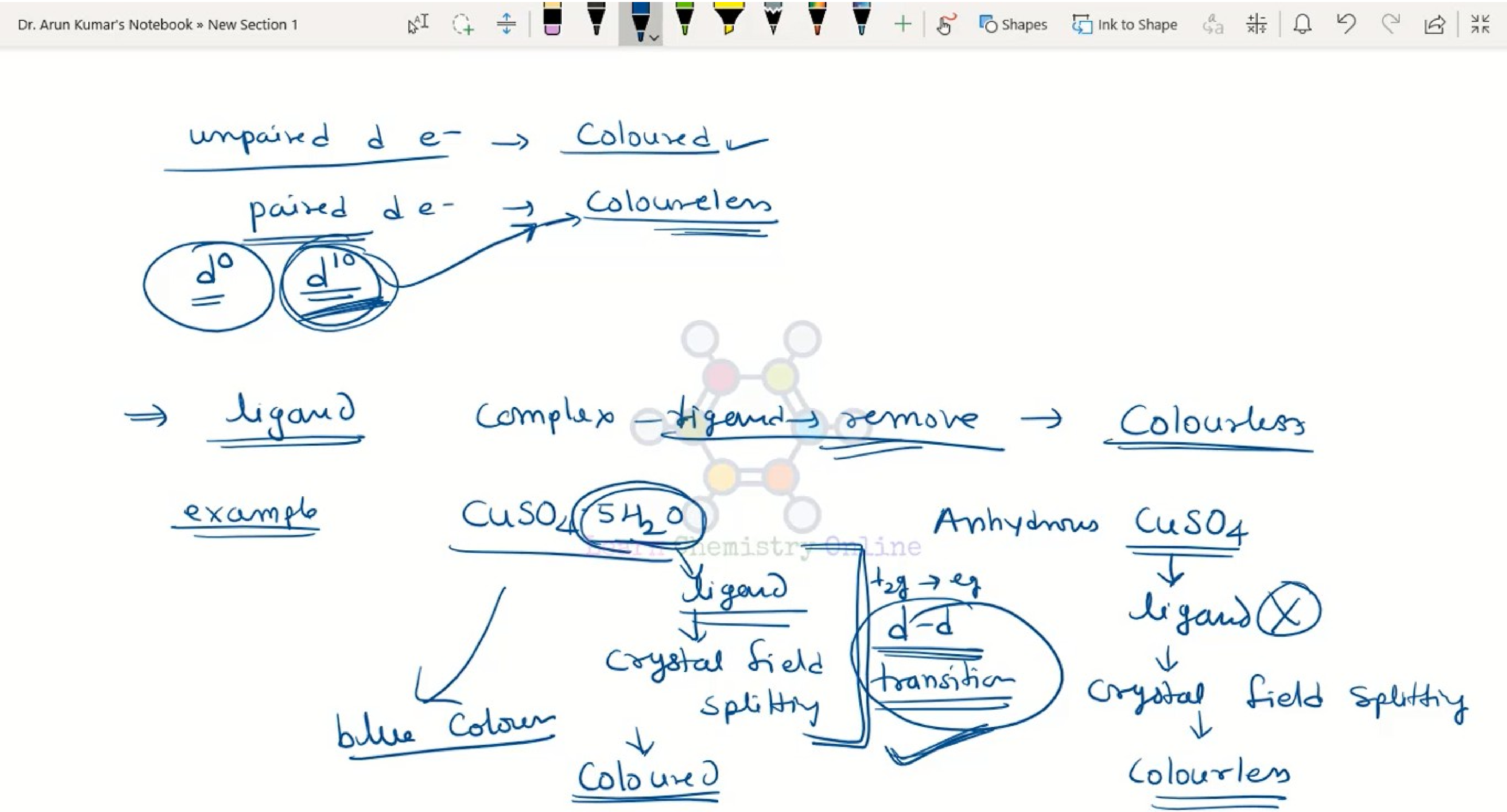
E.S. — — e_g

G.S ↑ — — t_{2g}

$\xrightarrow{h\nu}$

E.S. ↑ — e_g

G.S. — — — t_{2g}



unpaired d e⁻ → Coloured ✓

paired d e⁻ → Colourless

d^0 d^{10}

⇒ ligand

complex − ligand → remove → Colourless

example

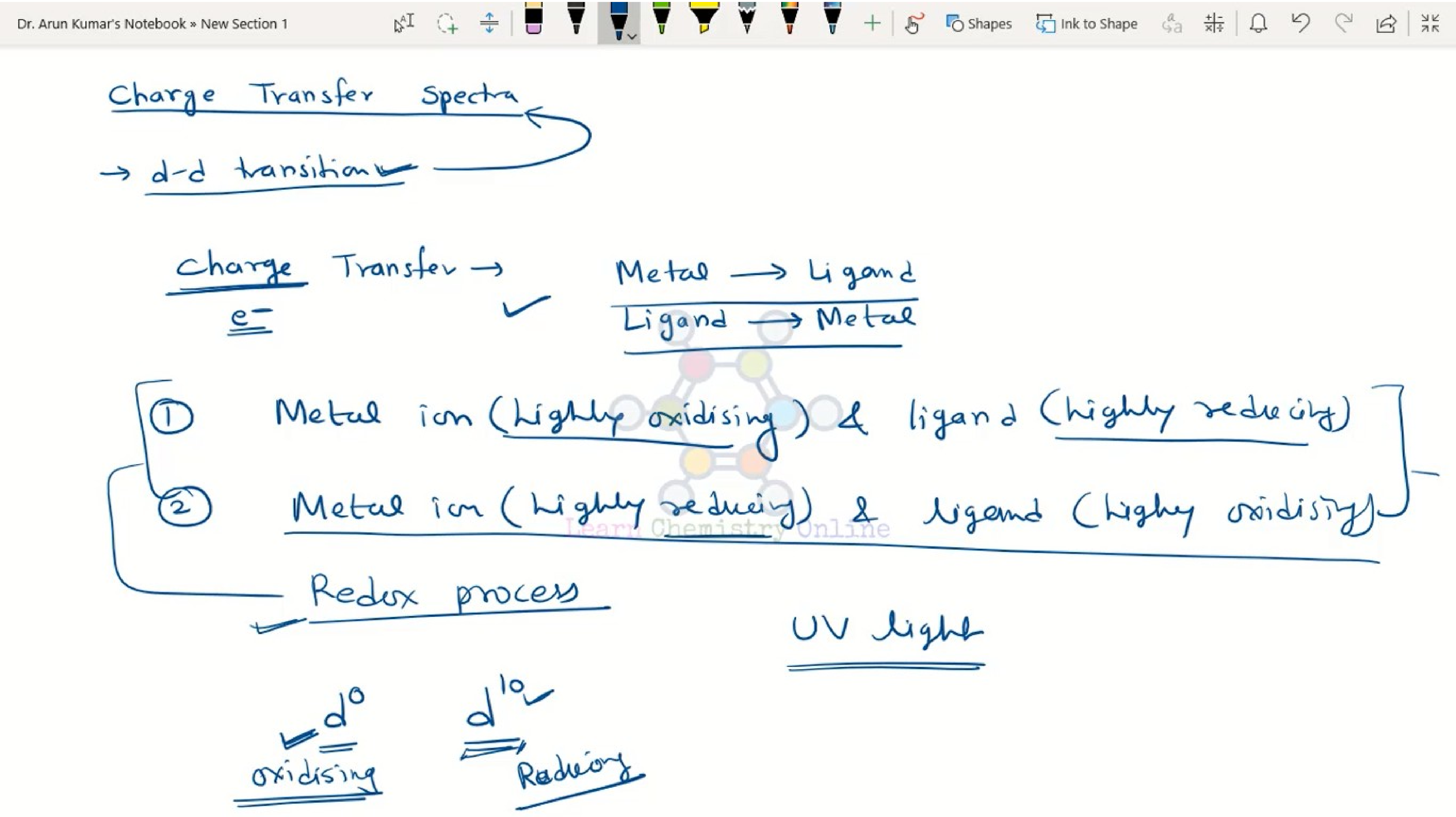
$CuSO_4 \cdot 5H_2O$ → ligand → crystal field splitting → Coloured

blue Colour

$t_{2g} \rightarrow e_g$

d−d transition

Anhydrous $CuSO_4$ → ligand ☒ → crystal field splitting → Colourless



Charge Transfer Spectra

→ d-d transition ✓

Charge Transfer →
e^-

✓

Metal → Ligand
Ligand → Metal

① Metal ion (highly oxidising) & ligand (highly reducing)

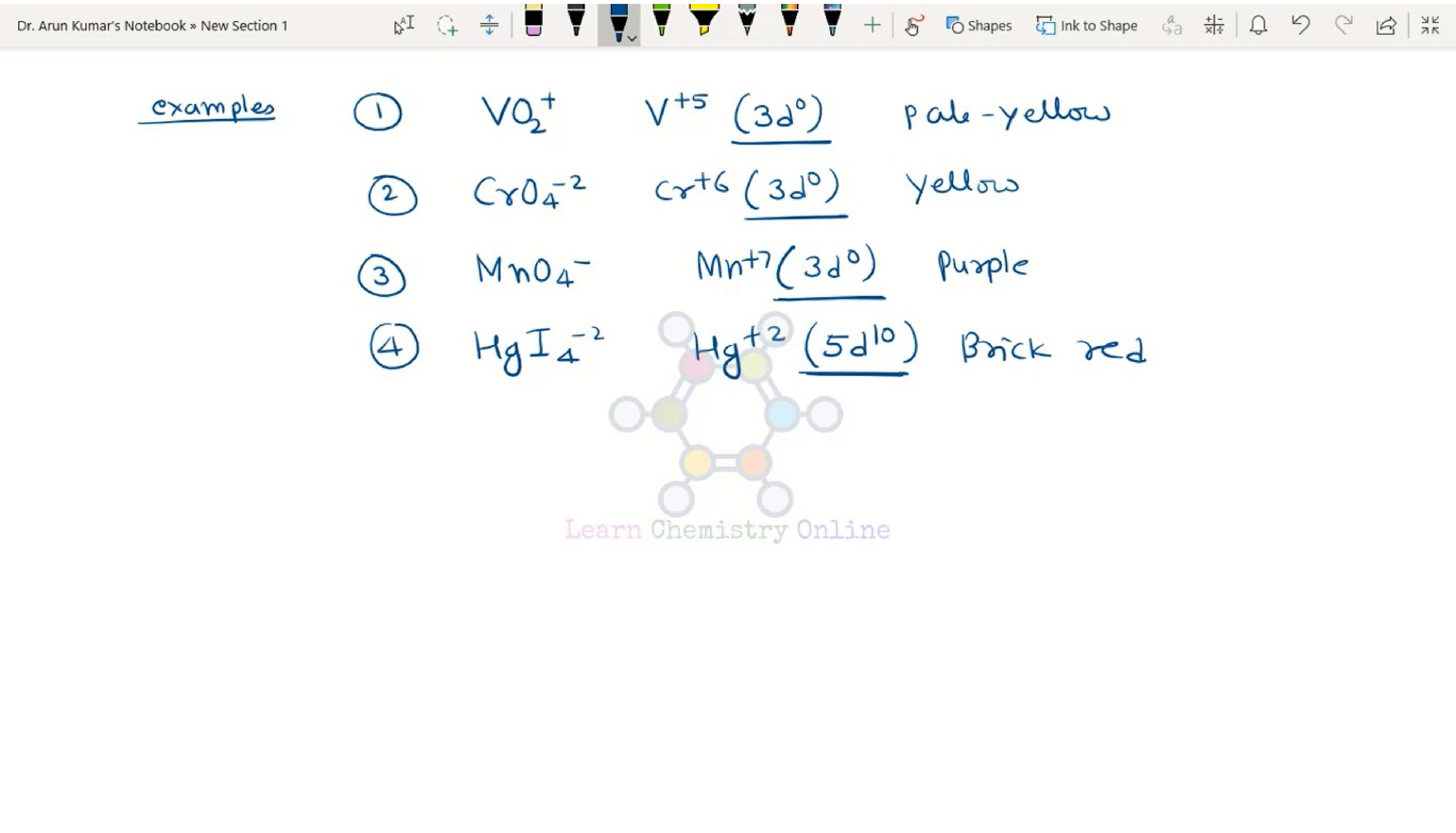
② Metal ion (highly reducing) & ligand (highly oxidising)

✓ Redox process

UV light

✓ d^0
oxidising

d^{10} ✓
Reducing



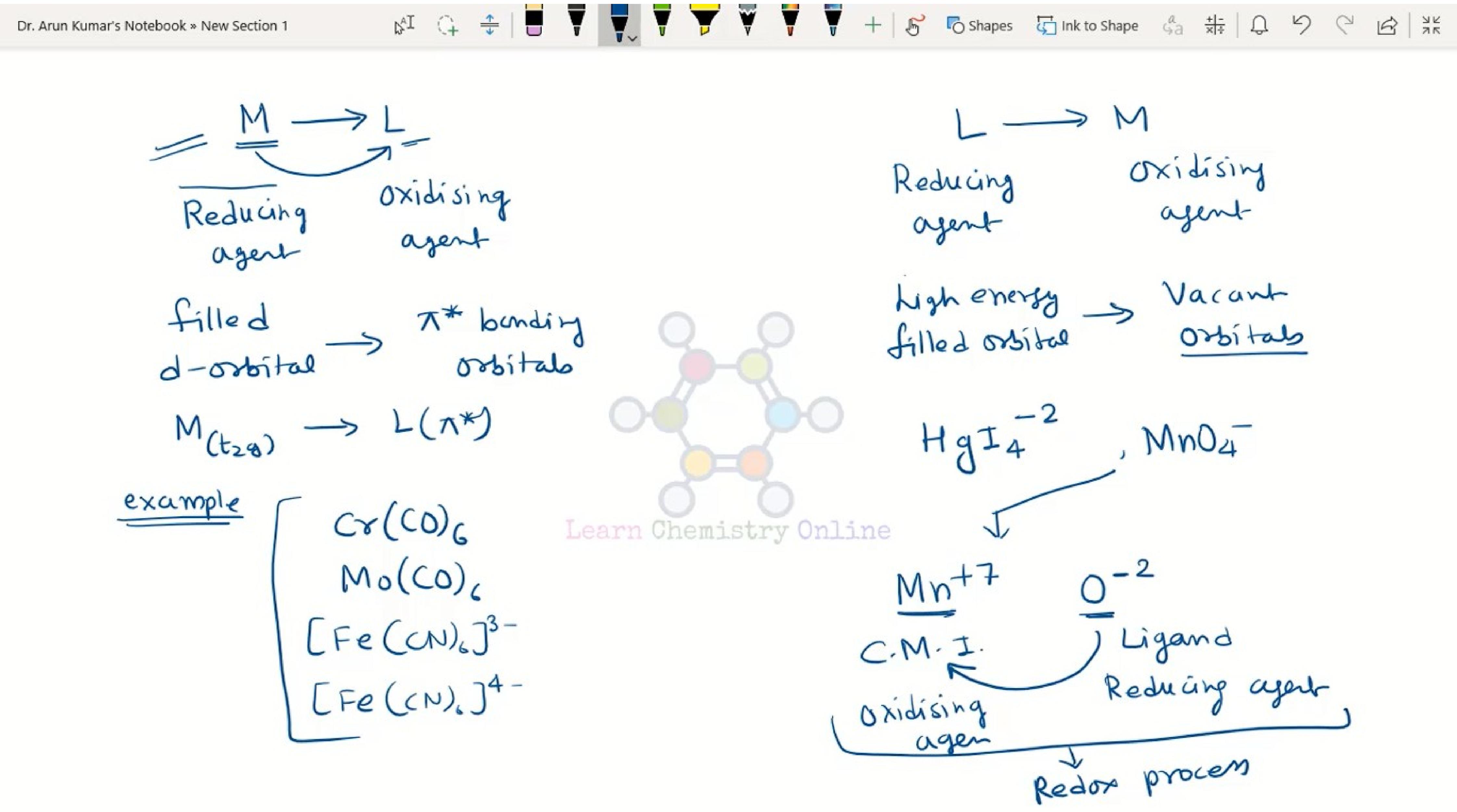
examples

① VO_2^+ V^{+5} $\underline{(3d^0)}$ pale-yellow

② CrO_4^{-2} Cr^{+6} $\underline{(3d^0)}$ yellow

③ MnO_4^- Mn^{+7} $\underline{(3d^0)}$ purple

④ HgI_4^{-2} Hg^{+2} $\underline{(5d^{10})}$ Brick red



$\overset{=}{M} \longrightarrow \underset{-}{L}$

Reducing agent   Oxidising agent

filled d-orbital → π^* bonding orbitals

$M_{(t_{2g})} \longrightarrow L(\pi^*)$

example

$Cr(CO)_6$

$Mo(CO)_6$

$[Fe(CN)_6]^{3-}$

$[Fe(CN)_6]^{4-}$

$L \longrightarrow M$

Reducing agent   Oxidising agent

high energy filled orbital → Vacant orbitals

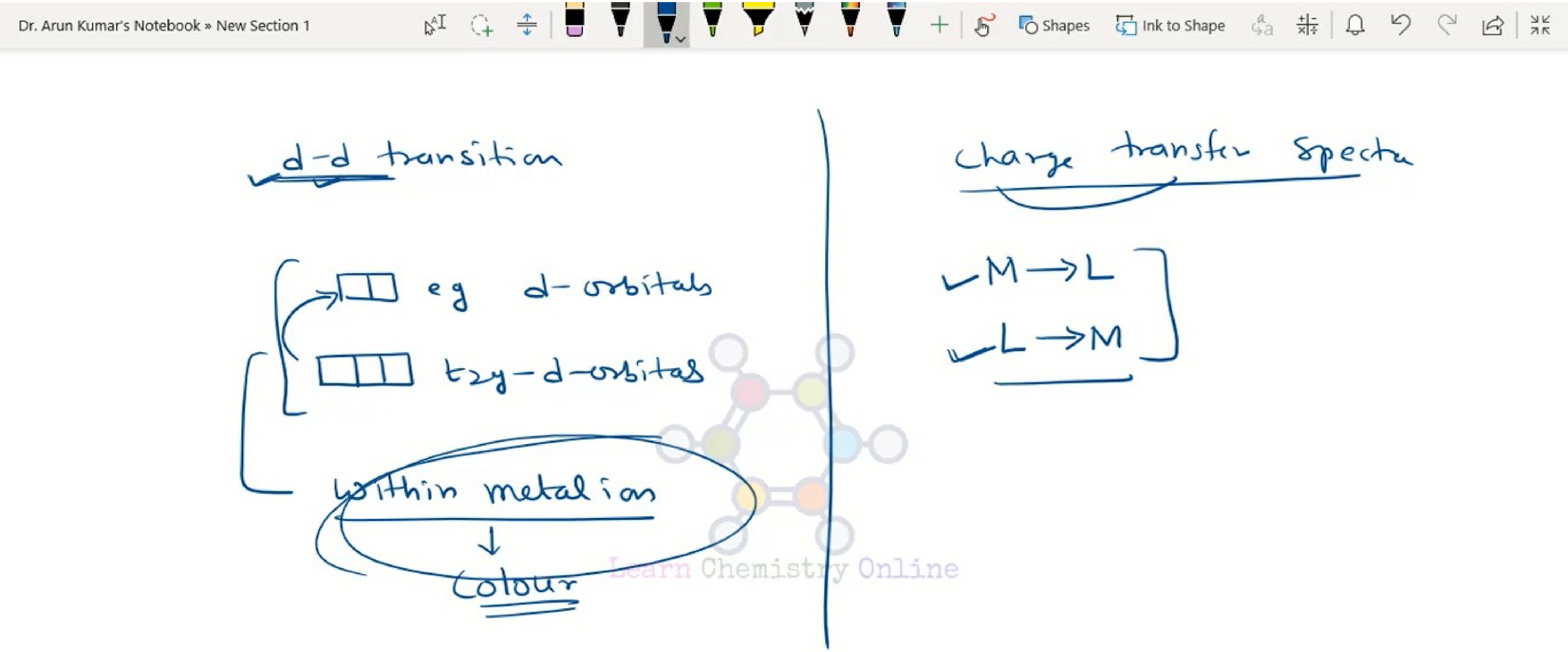
HgI_4^{-2} , MnO_4^-

Mn^{+7} O^{-2}

C.M.I.   Ligand

Oxidising agen   Reducing agent

Redox process



d-d transition

e_g d-orbitals

t_{2g}-d-orbitals

within metal ion

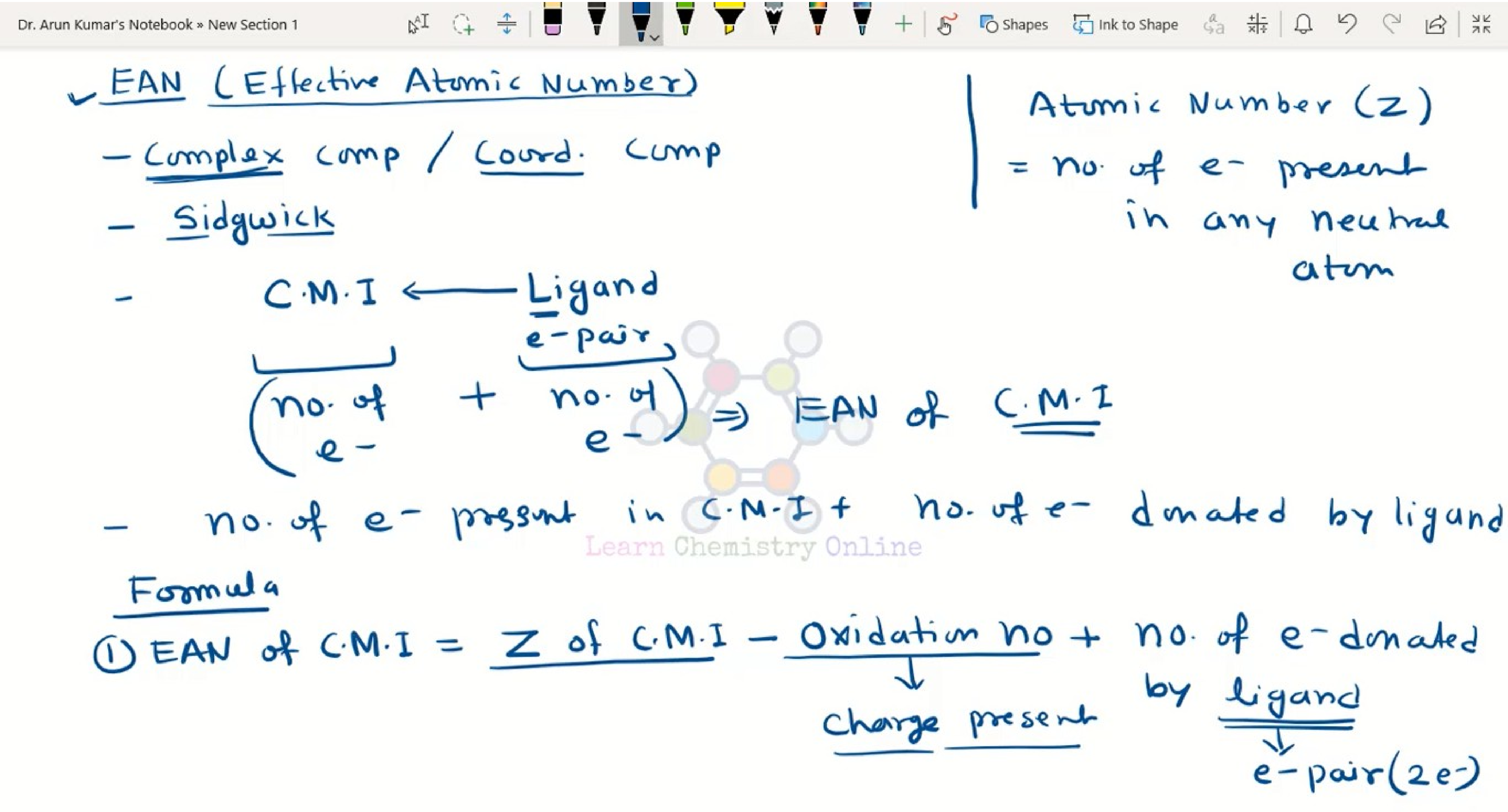
↓

Colour

Charge transfer Spectra

M → L

L → M



✓ EAN (Effective Atomic Number)

- Complex comp / Coord. Comp
- Sidgwick
- $$C \cdot M \cdot I \xleftarrow{} \underset{\text{e-pair}}{\text{Ligand}}$$

$$\left(\overbrace{\text{no. of e-}} + \overbrace{\text{no. of e-}}\right) \Rightarrow \text{EAN of } C \cdot M \cdot I$$

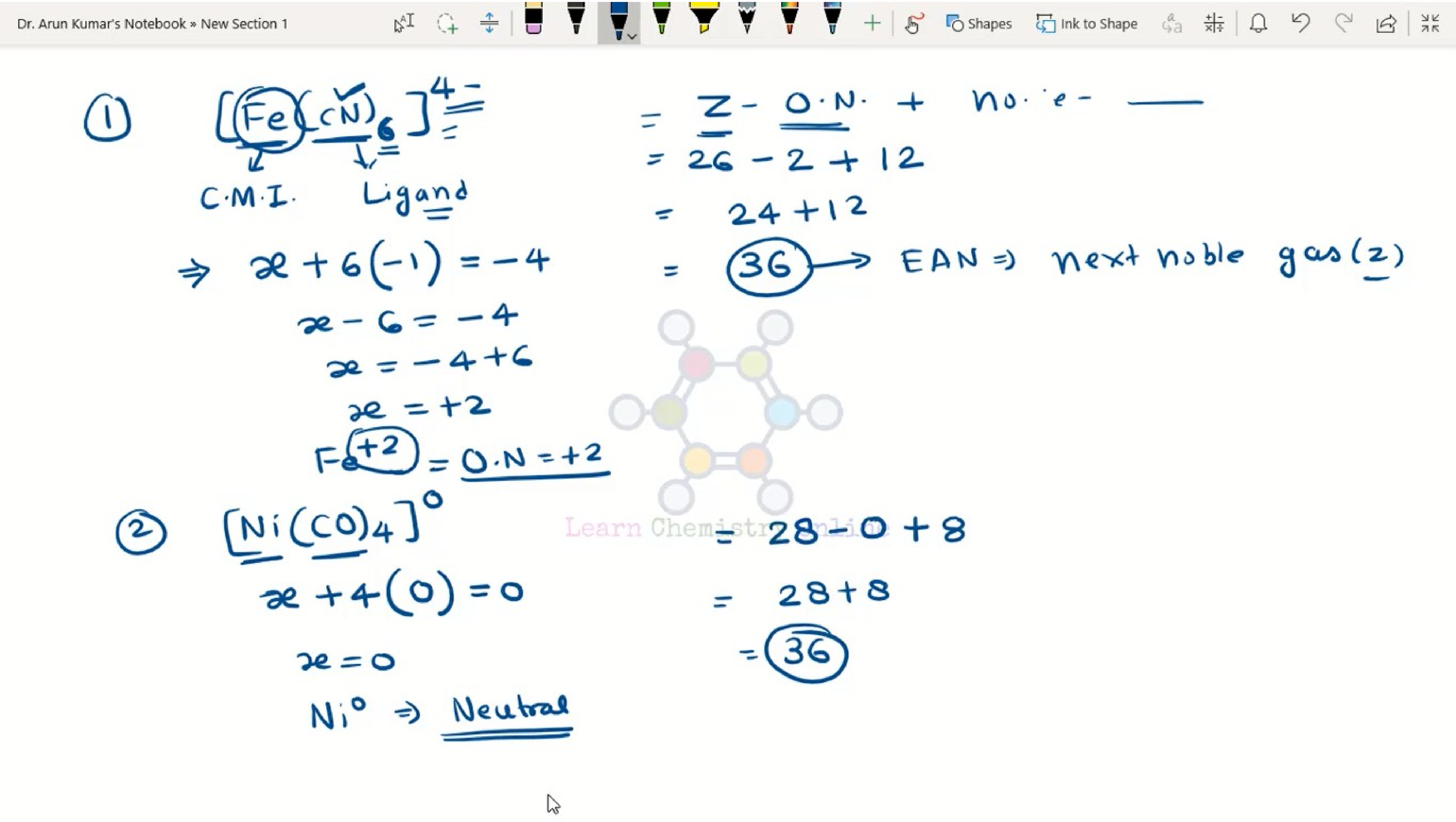
- no. of e- present in C.M.I + no. of e- donated by ligand

Atomic Number (Z)

= no. of e- present in any neutral atom

Formula

① $$\text{EAN of C.M.I} = \text{Z of C.M.I} - \underset{\substack{\downarrow \\ \text{Charge present}}}{\text{Oxidation no}} + \text{no. of e- donated by } \underset{\substack{\downarrow \\ \text{e-pair (2e-)}}}{\text{ligand}}$$



① $[\boxed{Fe}(\underline{CN})_6]^{4-}$

$\downarrow$ C.M.I. $\quad\downarrow$ Ligand

$\Rightarrow x + 6(-1) = -4$

$x - 6 = -4$

$x = -4 + 6$

$x = +2$

$Fe^{\boxed{+2}} = \underline{O.N = +2}$

$= \underline{Z} - \underline{O.N.} + \text{no. } e^- \text{ ——}$

$= 26 - 2 + 12$

$= 24 + 12$

$= \boxed{36} \longrightarrow$ EAN $\Rightarrow$ next noble gas (z)

② $[\underline{Ni}(\underline{CO})_4]^0$

$x + 4(0) = 0$

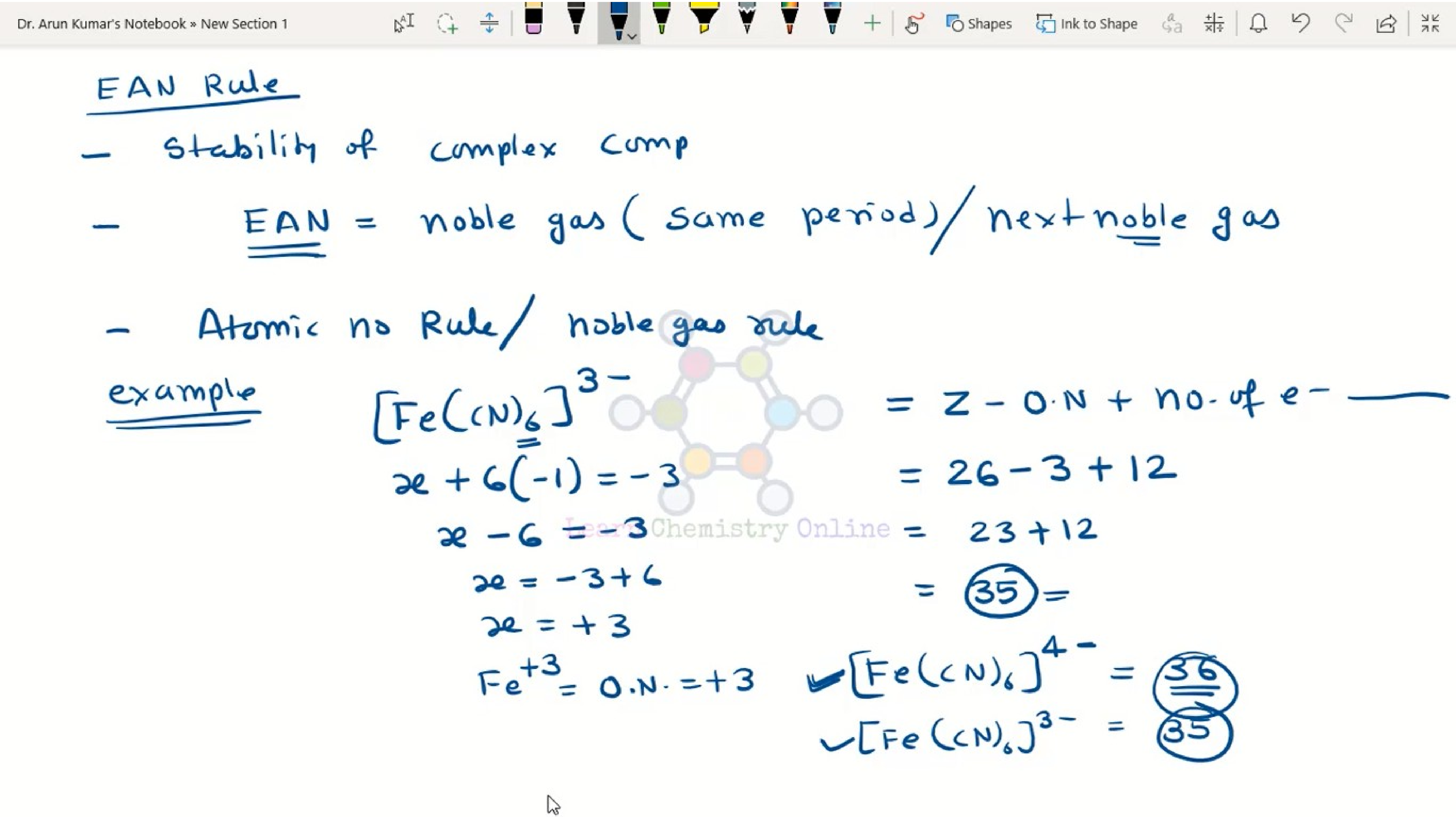
$x = 0$

$Ni^0 \Rightarrow \underline{\underline{\text{Neutral}}}$

$= 28 - 0 + 8$

$= 28 + 8$

$= \boxed{36}$



EAN Rule

- Stability of complex comp
- $\underline{\underline{EAN}}$ = noble gas (same period) / next noble gas
- Atomic no Rule / noble gas rule

example

$[Fe(\underline{\underline{CN}})_6]^{3-}$ = Z − O.N + no. of e⁻ ——

$x + 6(-1) = -3$ = 26 − 3 + 12

$x - 6 = -3$ = 23 + 12

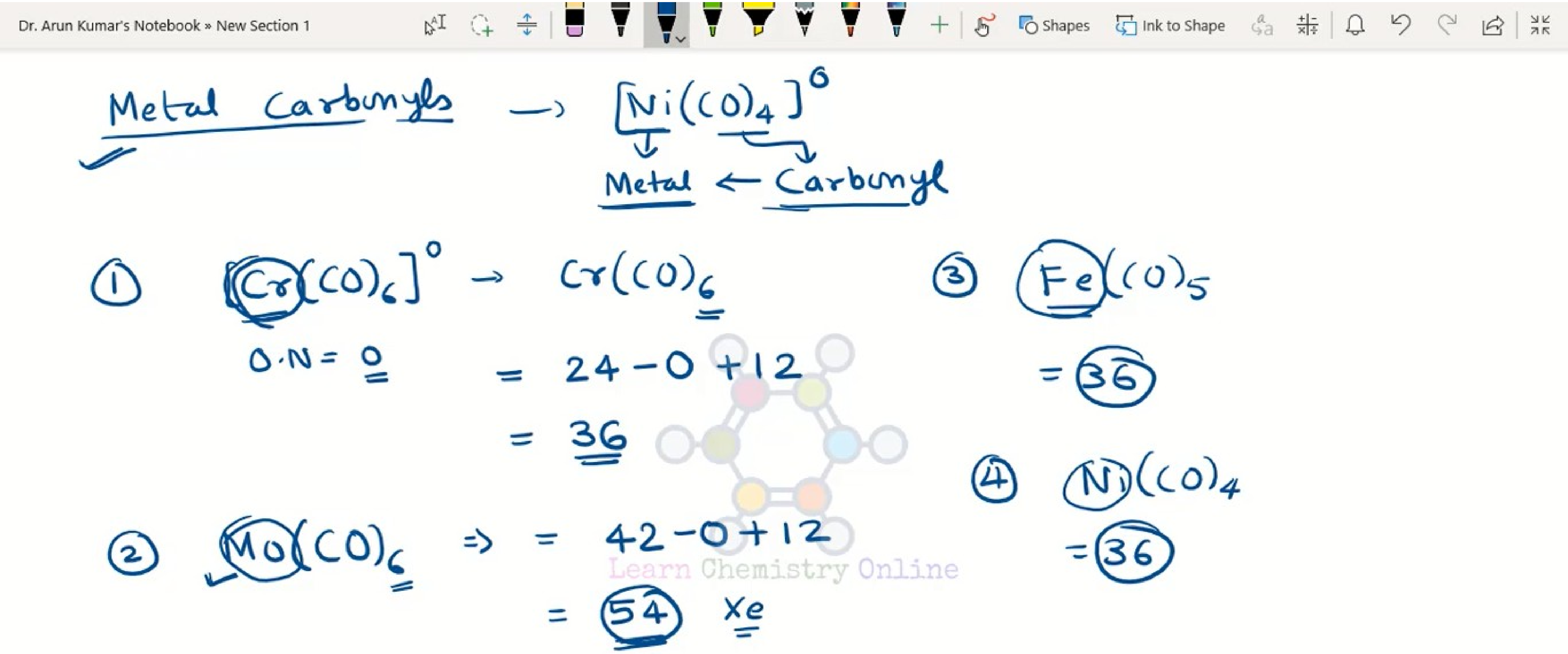
$x = -3 + 6$ = $\boxed{35}$ =

$x = +3$

$Fe^{+3} = O.N. = +3$

✓ $[Fe(CN)_6]^{4-} = \boxed{\underline{\underline{36}}}$

✓ $[Fe(CN)_6]^{3-} = \boxed{35}$



Metal Carbonyls

$\longrightarrow [Ni(CO)_4]^0$

Metal ← Carbonyl

① $[Cr(CO)_6]^0 \rightarrow Cr(CO)_6$

O.N = 0

= 24 − 0 + 12

= 36

② $Mo(CO)_6$ ⇒ = 42 − 0 + 12

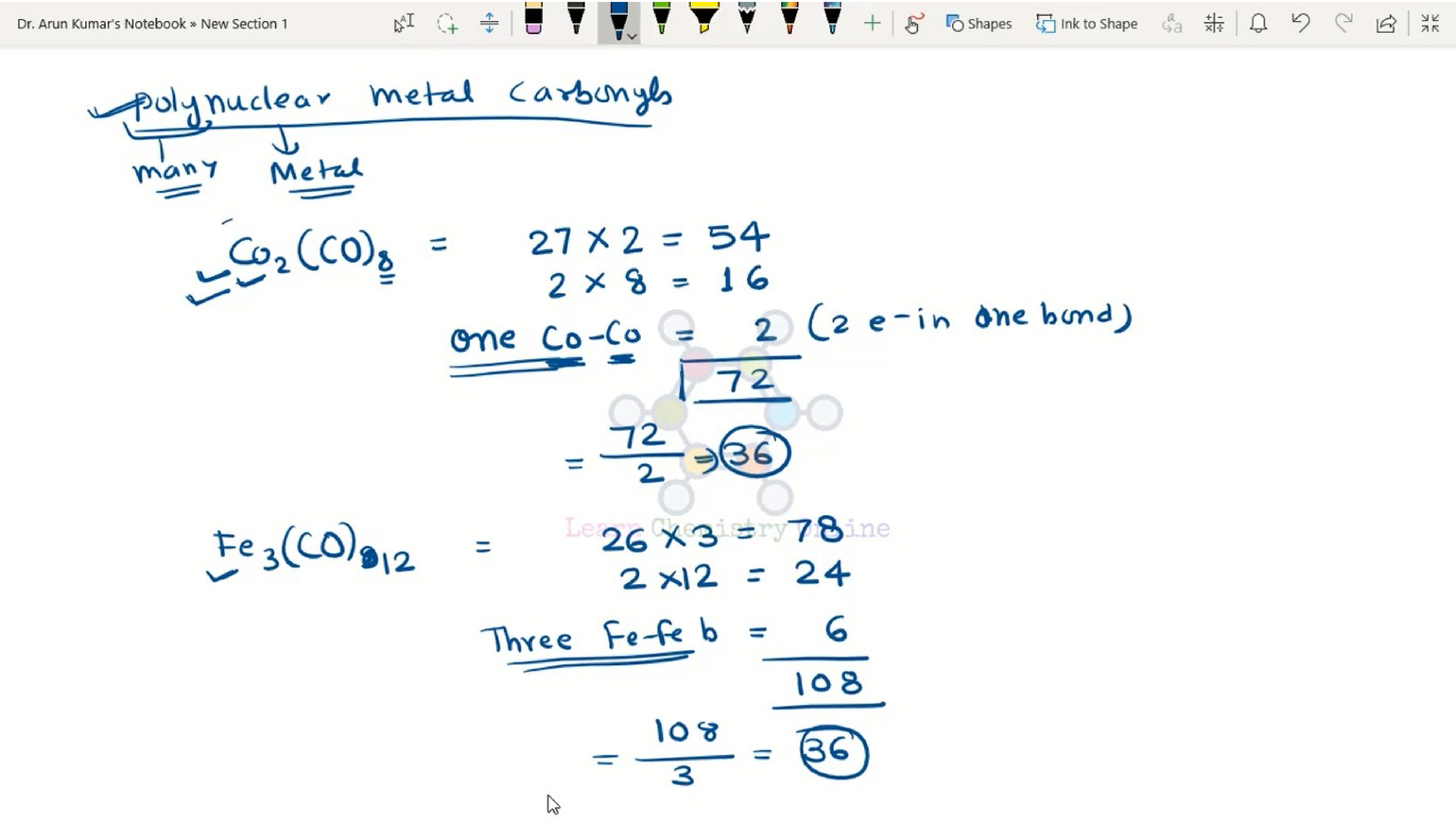
= $\boxed{54}$ Xe

③ $Fe(CO)_5$

= $\boxed{36}$

④ $Ni(CO)_4$

= $\boxed{36}$



Polynuclear metal carbonyls

Poly → many

nuclear → Metal

$Co_2(CO)_8$ = $27 \times 2 = 54$

$2 \times 8 = 16$

One Co-Co = 2 (2 e- in one bond)

72

$= \frac{72}{2} \Rightarrow \boxed{36}$

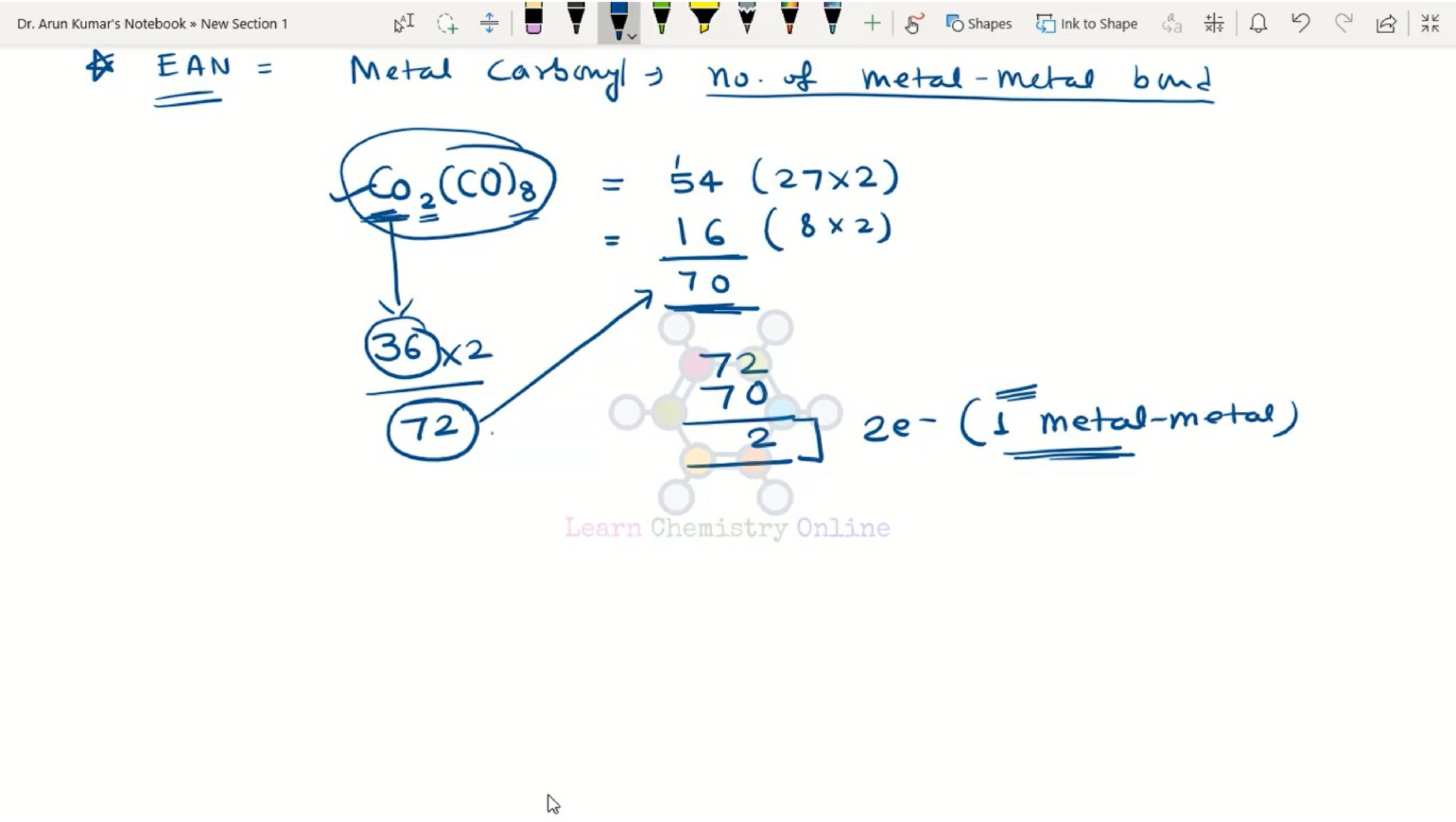
$Fe_3(CO)_{12}$ = $26 \times 3 = 78$

$2 \times 12 = 24$

Three Fe-Fe b = 6

108

$= \frac{108}{3} = \boxed{36}$



★ EAN = Metal Carbonyl ⇒ no. of metal-metal bond

$Co_2(CO)_8$ = 54 (27×2)

= 16 (8×2)

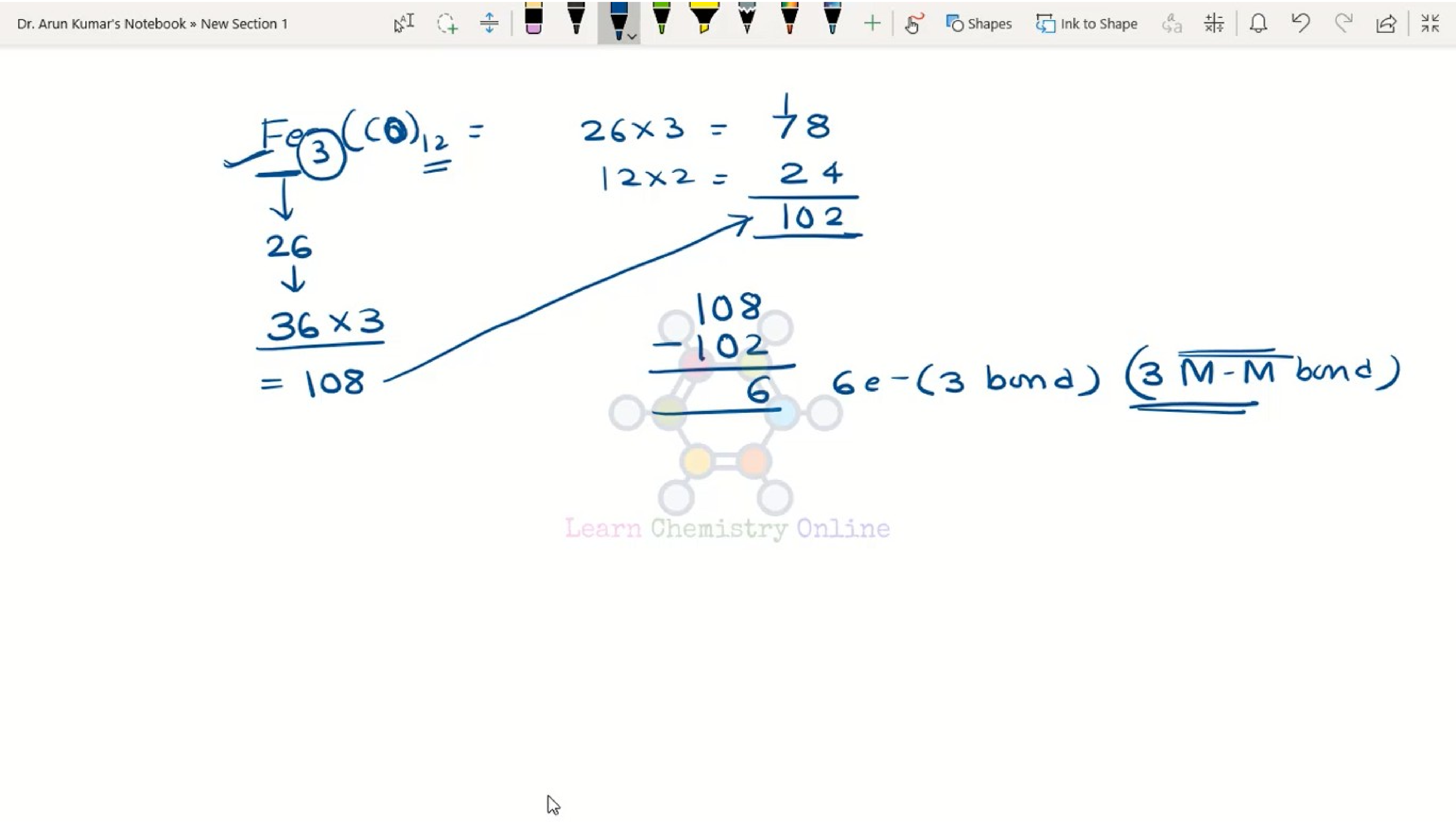
$\overline{70}$

36 ×2

$\overline{72}$ → 70

$$\begin{array}{r} 72 \\ 70 \\ \hline 2 \end{array}$$

2e⁻ (1 metal-metal)



$Fe_3(CO)_{12} =$

↓

26

↓

$$\begin{array}{r} 36 \times 3 \\ \hline = 108 \end{array}$$

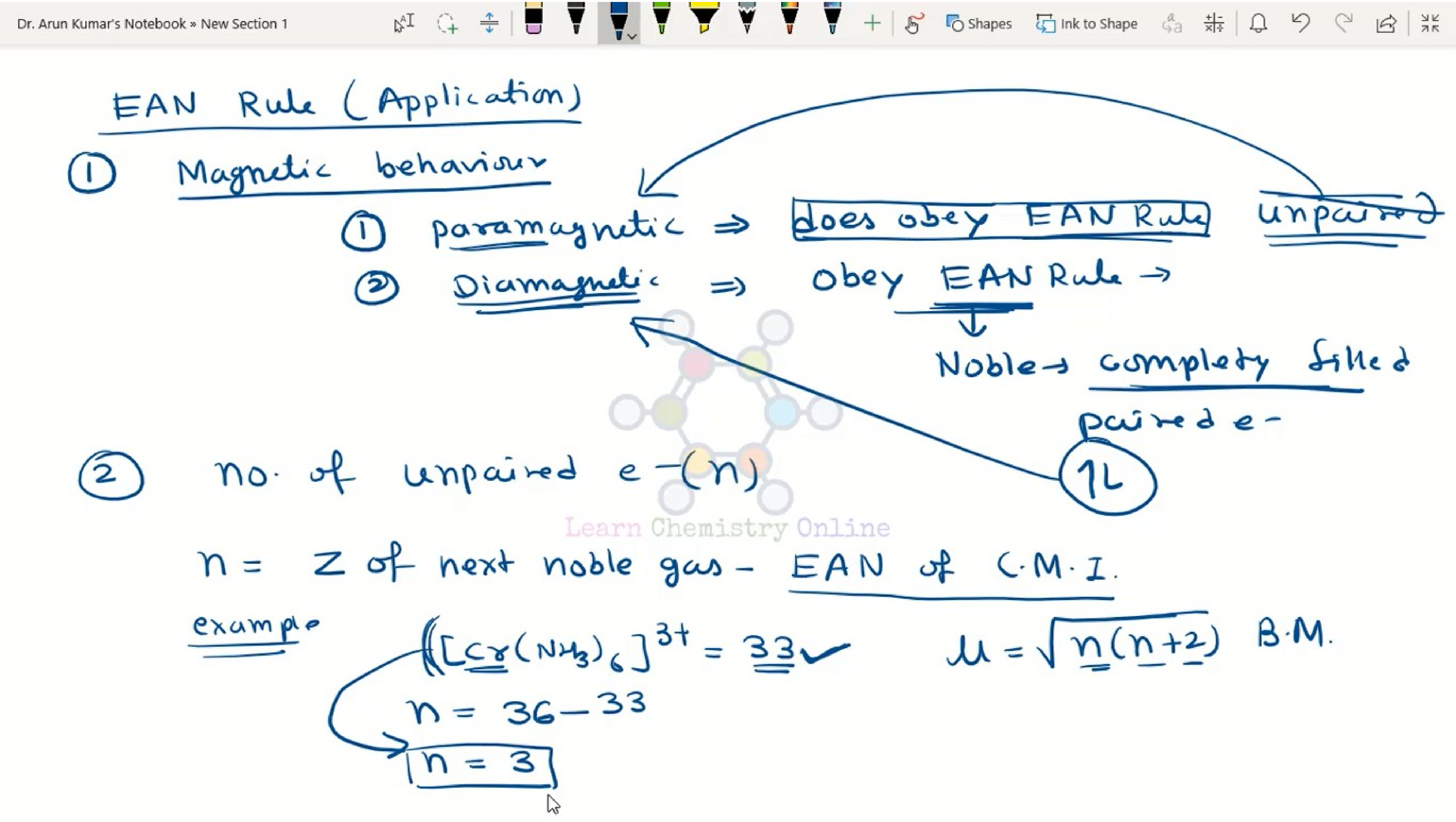
$26 \times 3 = 78$

$12 \times 2 = 24$

$$\begin{array}{r} 102 \\ \hline \end{array}$$

$$\begin{array}{r} 108 \\ -102 \\ \hline 6 \\ \hline \end{array}$$

6e − (3 bond) (3 M-M bond)



EAN Rule (Application)

① **Magnetic behaviour**

① paramagnetic ⇒ $\boxed{\text{does obey EAN Rule}}$ unpaired

② Diamagnetic ⇒ obey EAN Rule →

↓

Noble → completely filled

paired e-

↑↓

② no. of unpaired e- (n)

n = Z of next noble gas - EAN of C.M.I.

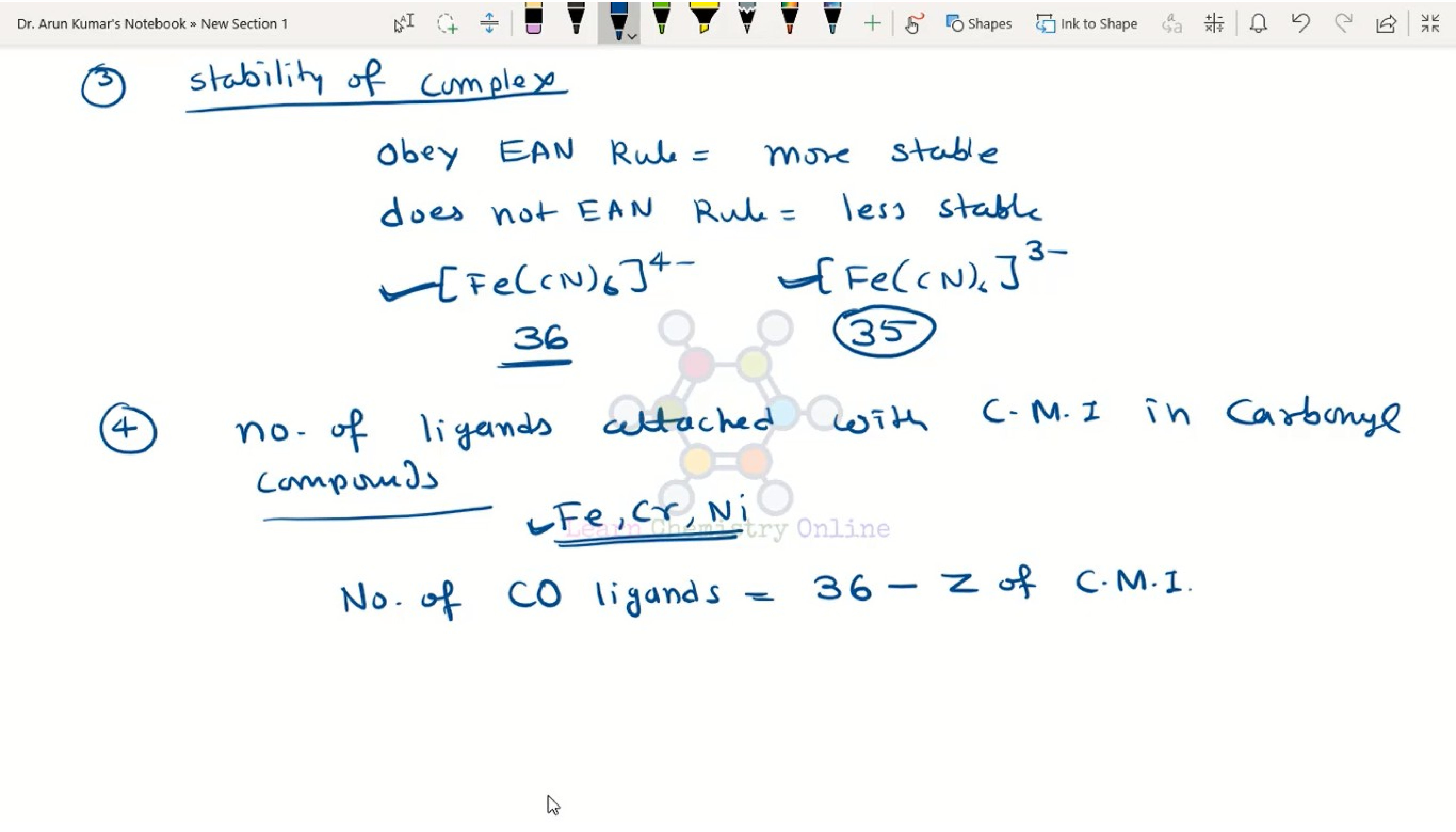
example

$[Cr(NH_3)_6]^{3+} = 33$ ✓

$\mu = \sqrt{n(n+2)}$ B.M.

$n = 36 - 33$

$\boxed{n = 3}$



③ stability of complex

Obey EAN Rule = more stable

does not EAN Rule = less stable

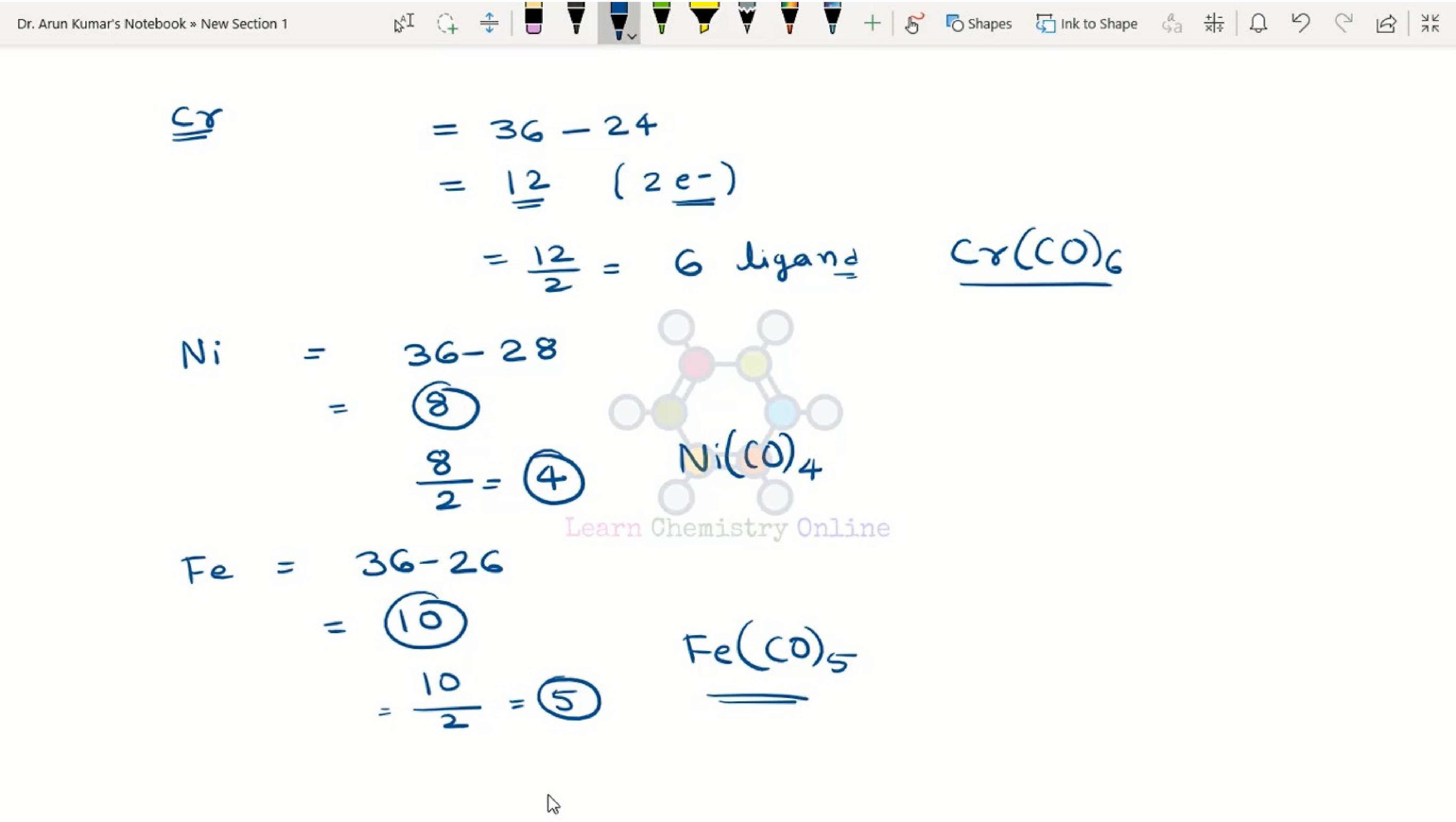
✓ $[Fe(CN)_6]^{4-}$ ✓ $[Fe(CN)_6]^{3-}$

$\underline{36}$ ㉟

④ no. of ligands attached with C.M.I in Carbonyl compounds

✓ $\underline{Fe, Cr, Ni}$

No. of CO ligands = 36 − Z of C.M.I.



Cr $= 36 - 24$

$= \underline{\underline{12}} \quad (2 \underline{\underline{e^-}})$

$= \frac{12}{2} = 6$ ligand

$\underline{Cr(CO)_6}$

Ni $= 36 - 28$

$= \boxed{8}$

$\frac{8}{2} = \boxed{4}$

$Ni(CO)_4$

Fe $= 36 - 26$

$= \boxed{10}$

$= \frac{10}{2} = \boxed{5}$

$\underline{\underline{Fe(CO)_5}}$