

B.Sc (SIXTH SEMESTER) EXAMINATION, 2013
CHEMISTRY

PAPER: CBT-603

(PHYSICAL CHEMISTRY - A MOLECULAR APPROACH)

TIME ALLOWED: THREE HOURS

MAXIMUM MARKS: 30

NOTE: SECTION A IS COMPULSORY AND ANSWER ANY FIVE QUESTIONS FROM SECTION B.

SECTION - A

10x1=10

(SHORT ANSWER TYPE QUESTIONS)

NOTE: ANSWER ALL QUESTIONS. EACH QUESTION CARRIES 1 MARK.

Q1 i) DIFFERENTIATE BETWEEN EXPECTATION VALUE AND NORMALIZATION FOR A QUANTUM MECHANICAL WAVE FUNCTION

ANS 1 i) EXPECTATION VALUE OF AN OPERATOR A_{op} IS A STATISTICAL AVERAGE OF THE OBSERVED VALUES OF THE QUANTITY FOR WHICH THE OPERATOR A_{op} STANDS FOR ∞ WITH REFERENCE TO A QUANTUM MECHANICAL WAVE FUNCTION ψ

EXPECTATION VALUE CAN BE REPRESENTED AS

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d\tau}{\int \psi^* \psi d\tau} \quad \text{--- (1)}$$

CONDITION OF NORMALIZATION REPRESENTS INTEGRATION OVER THE WHOLE CONFIGURATION SPACE THE PROBABILITY OF FINDING THE PARTICULAR SYSTEM IN THE SMALL VOLUME ELEMENT

$$\therefore \int \psi^* \psi d\tau = N \quad \text{OR} \quad \frac{1}{N} \int \psi^* \psi d\tau = 1 \quad \text{--- (2)}$$

WHERE $\frac{1}{N^{1/2}}$ IS KNOWN AS THE NORMALIZATION CONSTANT.

★ EVEN THE TWO EQUATIONS IS ACCEPTABLE

SHORT ANSWER TYPE QUESTIONS
CONTINUED

Q1 ii) WHAT ARE THE BOUNDARY CONDITIONS FOR A PARTICLE IN A ONE DIMENSIONAL BOX?

ANS1 ii) CONSIDERING A PARTICLE IN ONE DIMENSIONAL BOX OF LENGTH l

$$\left. \begin{array}{l} V_x = 0 \text{ WITHIN THE BOX} \\ V_x = \infty \text{ OUTSIDE THE BOX} \end{array} \right\} \text{ WHERE } V \text{ REPRESENTS THE POTENTIAL ENERGY}$$

CONVERSLY

$$\psi = 0 \text{ AT } x = 0 \text{ AND } x = l$$

WHERE ψ IS THE QUANTUM MECHANICAL WAVE FUNCTION REPRESENTING THE PARTICLE

★ BOTH ANSWERS ARE ACCEPTABLE.

Q1 iii) WRITE DOWN THE CORRECT ORDER OF ENERGY LEVELS WITH S-P INTERACTIONS. (BASED ON MOT OF A HOMO-NUCLEAR DIATOMIC MOLECULE)

ANS1 iii) $\sigma_{1s} \sigma_{1s}^* \sigma_{2s} \sigma_{2s}^* \pi_{2p} \sigma_{2p} \pi_{2s}^* \sigma_{2p}^*$

THE ASCENDING ORDER OF ENERGY LEVELS WITH S-P INTERACTION

Q1 iv) WHAT DO YOU MEAN BY ENERGY MINIMIZATION?

ANS1 iv) IT IS A MATHEMATICAL TECHNIQUE USED TO COMPUTE THE EQUILIBRIUM CONFIGURATION OF MOLECULES.

★ ANY VARIATION OF THE ABOVE STATEMENT IS ACCEPTABLE

Q1 v) HOW CAN YOU DEFINE A MACROSYSTEM?

ANS1 v) WE LOOK AT A THERMODYNAMIC SYSTEM AS A MACROSYSTEM i.e. IT CONSISTS OF A LARGE NUMBER OF MOLECULES. SUCH THAT IN ESTABLISHING THE VARIOUS THERMODYNAMIC FUNCTIONS WE DO NOT NEED TO CONCERN OURSELVES WITH THE COMPOSITION OF A SYSTEM.

Q1 vi) WHAT IS STATISTICAL THERMODYNAMICS?

ANS1 vi) STATISTICAL THERMODYNAMICS CONCERNS ITSELF WITH THE NUMBER OF WAYS THE MOLECULES ARE DISTRIBUTED OVER THE AVAILABLE QUANTUM MECHANICAL ENERGY STATES SUBJECT TO THE CONSTANTANCY OF THE ENERGY OF THE SYSTEM.

SHORT ANSWER TYPE QUESTIONSCONTINUED

Q1 vii) WHAT ARE NORMAL MODES OF VIBRATION?

ANS vii) CONSIDERING A MOLECULE CONTAINING N ATOMS IT POSSESSES $3N$ DEGREES OF FREEDOM AND CONSEQUENTLY FOR A NON LINEAR MOLECULE

THERE ARE $3N-6$ FUNDAMENTAL VIBRATIONS

AND FOR A LINEAR MOLECULE

$3N-5$ FUNDAMENTAL VIBRATIONS

°° CONSIDERING H_2O ; $N=3$ °° IT POSSESSES 3 VIBRATIONAL MODES

THESE THREE VIBRATIONAL MOTIONS ARE ALSO REFERRED TO AS

NORMAL MODES OF VIBRATION

★ EVEN A DIAGRAMATIC REPRESENTATION OF H_2O VIBRATIONAL MODES IS ACCEPTABLE

Q1 viii) ELECTRONIC SPECTRA OF DIATOMIC MOLECULES INVOLVE WHAT TYPES OF TRANSITIONS?

ANS viii) ELECTRONIC TRANSITIONS INVOLVE EXCITING AN ELECTRON FROM ONE PRINCIPAL QUANTUM STATE TO ANOTHER.

FOR EXAMPLE IN THE CASE OF COMPOUNDS CONTAINING CARBONYL GROUP

$n \rightarrow \pi^*$ TRANSITIONS ARE OBSERVED.

Q1 ix) ETHANOL AND METHANOL WILL BE ASSOCIATED WITH HOW MANY DIFFERENT TYPES OF SIGNALS IN AN 1H NMR SPECTRA?

ANS ix) CH_3CH_2OH — 3 SIGNALS

ETHANOL

CH_3OH — 2 SIGNALS

Q1 x) WHAT TYPES OF SOLVENTS CAN YOU USE AS NMR SOLVENTS?

ANS x) SOLVENT SHOULD COMPLETELY DISSOLVE THE COMPOUND TO BE ANALYZED AND SHOULD BE DEUTERATED EXAMPLE $CDCl_3$, D_2O ETC.

SECTION B

5 x 4 = 20

LONG ANSWER TYPE QUESTIONS

NOTE: ANSWER ANY FIVE QUESTIONS. EACH QUESTION CARRIES 4 MARKS

Q2 WHAT ARE THE POSTULATES NECESSARY FOR THE DERIVATION OF SCHRÖDINGER WAVE EQUATION?

ANS 2 THE POSTULATES ARE AS FOLLOWS

- 1) FOR EVERY STATE OF A TIME INDEPENDENT PHYSICAL SYSTEM, A FUNCTION ψ OF THE COORDINATES CAN BE WRITTEN.
- 2) THE FUNCTION ψ MUST BE SINGLE VALUED, CONTINUOUS AND FINITE THROUGHOUT THE CONFIGURATION SPACE. IT MUST BE QUADRATICALLY INTEGRABLE. IF THE PROBLEM UNDER STUDY DOES NOT INVOLVE ANY DISCONTINUITY AT THE BOUNDARY, THE FIRST DERIVATIVE OF THE FUNCTION ψ MUST ALSO BE CONTINUOUS
- 3) CORRESPONDING TO EVERY OBSERVABLE QUANTITY IN CLASSICAL MECHANICS E.g. POSITION, MOMENTUM, ENERGY, THERE CORRESPONDS A LINEAR MATHEMATICAL OPERATOR.
- 4) FOR A GIVEN OPERATOR A_{op} IT IS POSSIBLE TO WRITE

$$A_{op} \psi = a \psi \quad \text{WHERE } a \rightarrow \text{EIGEN VALUE}$$

Q3 GIVEN THE RELATION BELOW PROVE THAT:

- a) EIGEN VALUES OF A HERMITIAN OPERATOR ARE ALL REAL.
- b) THE NONDEGENERATE EIGEN FUNCTIONS OF A HERMITIAN OPERATOR ARE ORTHOGONAL TO EACH OTHER i.e. THE EXPRESSION $\langle \psi_a | \psi_b \rangle = 0$ HOLDS GOOD.

$$\int \psi_n^* A_{op} \psi_m d\tau = \int \psi_m^* A_{op}^* \psi_n d\tau$$

ANS 3 a) LET ψ_n BE ONE OF THE EIGENFUNCTIONS OF THE OPERATOR A_{op} AND LET α_n BE THE CORRESPONDING EIGENVALUE. WE WILL HAVE.

$$A_{op} \psi_n = \alpha_n \psi_n \quad \text{--- (1)}$$

MULTIPLYING BOTH SIDES OF EQUATION 1 BY ψ_n^* AND THEN INTEGRATING WE GET

$$\int \psi_n^* A_{op} \psi_n d\tau = \alpha_n \int \psi_n^* \psi_n d\tau \quad \text{--- (2)}$$

THE COMPLEX CONJUGATE OF EQUATION (2) MUST ALSO BE VALID THUS WE HAVE

$$\int \psi_n A_{op}^* \psi_n^* d\tau = \alpha_n^* \int \psi_n \psi_n^* d\tau \quad \text{--- (3)}$$

SINCE A_{op} IS HERMITIAN L.H.S OF EQU. 2 AND 3 ARE EQUAL
(GIVEN)

$$\alpha_n \int \psi_n^* \psi_n d\tau = \alpha_n^* \int \psi_n \psi_n^* d\tau \quad \text{--- (4)}$$

SINCE $\int \psi_n^* \psi_n d\tau$ IS NON ZERO; WE HAVE

$$\alpha_n = \alpha_n^* \quad \therefore \alpha \text{ IS REAL}$$

LONG ANSWER TYPE QUESTIONS
CONTINUED

ANS 3: CONTINUED

b) LET α_m AND α_n BE THE EIGEN VALUES OF THE FUNCTION ψ_m AND ψ_n RESPECTIVELY.

$$\therefore A_{op} \psi_m = \alpha_m \psi_m \quad - (1)$$

$$A_{op}^* \psi_n^* = \alpha_n \psi_n^* \quad - (2)$$

MULTIPLYING EQUATION 1 BY ψ_n^* AND INTEGRATING, WE GET

$$\int \psi_n^* A_{op} \psi_m = \alpha_m \int \psi_n^* \psi_m d\tau \quad - (3)$$

SIMILARLY MULTIPLYING EQU. 2 BY ψ_m , WE GET

$$\int \psi_m A_{op}^* \psi_n^* d\tau = \alpha_n \int \psi_n^* \psi_m d\tau \quad - (4)$$

SINCE GIVEN A_{op} IS HERMITIAN L.H.S. OF EQU. 3 AND 4 ARE EQUAL

$$\therefore \alpha_m \int \psi_n^* \psi_m d\tau = \alpha_n \int \psi_n^* \psi_m d\tau$$

SINCE α_m AND α_n ARE TWO DISTINCT EIGEN VALUES

$$\int \psi_n^* \psi_m d\tau = 0 \quad (\text{PROVED}).$$

Q4 IDENTIFY THE FACTORS INFLUENCING THE ENERGY LEVEL OF A MOLECULAR ORBITAL. BASED ON THESE FACTORS, DRAW THE RELATIVE ORDER OF ENERGIES OF MOLECULAR ORBITALS WITHOUT S-P INTERACTION.

ANS 4 THE TWO FACTORS INFLUENCING ENERGIES OF VARIOUS MOLECULAR ORBITALS ARE

- 1) THE TYPE OF ATOMIC ORBITALS FROM WHICH THE MOLECULAR ORBITAL IS BUILT UP.
- 2) THE EXTENT OF OVERLAP BETWEEN THE INVOLVED ORBITALS.

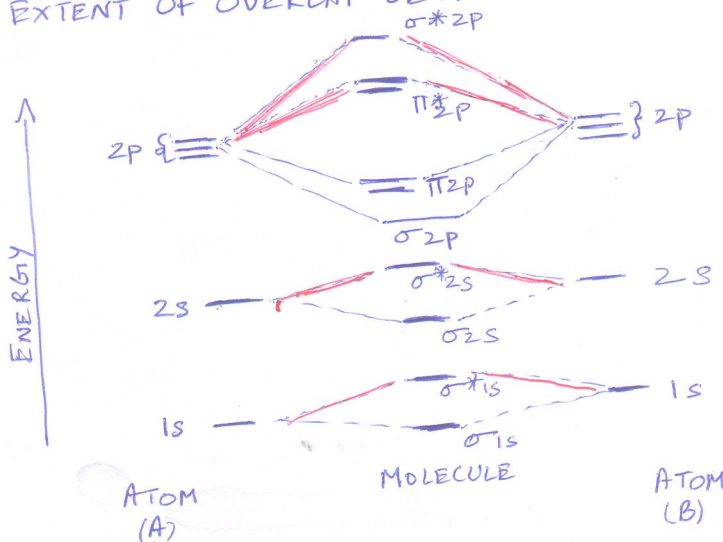


FIGURE 1. MOLECULAR ORBITAL DIAGRAM FOR MO'S WITHOUT S-P INTERACTION

LONG ANSWER TYPE QUESTIONS
CONTINUED

Q5 IDENTIFY THE KEY STEPS IN EVALUATION OF THE CONSTANT β USING THE EXPRESSION FOR INTERNAL ENERGY OF MONOATOMIC GAS AND THE BOLZMANN DISTRIBUTION LAW:

$$N_i = N g_i e^{\alpha} e^{-\beta E_i} \quad ; \quad U = \sum_i N_i E_i$$

ANS5 EVALUATION OF CONSTANT $\beta \rightarrow$

GIVEN $U = \sum_i N_i E_i$ — (1) [SINCE MONOATOMIC GAS HAS ONLY TRANSLATIONAL ENERGY]

SUBSTITUTING THE VALUE OF N_i

$$U = \frac{N}{q} \sum_i g_i E_i \exp(-\beta E_i) \quad \text{--- (2)}$$

SINCE $e^{\alpha} = \frac{1}{\sum_i g_i e^{-\beta E_i}}$

AND $N_i = \frac{N g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} = \frac{N}{q} g_i e^{-\beta E_i}$

NOW THE EXPRESSION OF E_i IN TERMS OF VELOCITY COMPONENT OF A MOLECULE IS

$$E_i = \frac{1}{2} m (v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \quad \text{--- (3)}$$

SUBSTITUTING 3 IN 2 WE GET

$$U = N \sum_i \frac{1}{2} m (v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \exp \left\{ -\frac{\beta m}{2} (v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \right\} \quad \text{--- (4)}$$

$$\sum_i \exp \left\{ -\frac{\beta m}{2} (v_{xi}^2 + v_{yi}^2 + v_{zi}^2) \right\}$$

SINCE TRANSLATIONAL ENERGY ARE VERY CLOSELY PLACED, THE VELOCITY COMPONENTS MAY BE CONSIDERED CONTINUOUS VARIABLES WITH SUMMATIONS REPLACED BY INTEGRALS

$$U = \frac{1}{2} m N \iiint_{-\infty}^{\infty} (v_x^2 + v_y^2 + v_z^2) \exp \left\{ -\frac{\beta m}{2} (v_x^2 + v_y^2 + v_z^2) \right\} dv_x dv_y dv_z \quad \text{--- (5)}$$

$$\iiint_{-\infty}^{\infty} \exp \left\{ -\frac{\beta m}{2} (v_x^2 + v_y^2 + v_z^2) \right\} dv_x dv_y dv_z$$

LONG ANSWER TYPE QUESTIONS
CONTINUED.

ANS5CONTINUED:

$$U = \frac{1}{2} m N \left[\frac{\int_{-\infty}^{\infty} v_x^2 \exp\left(-\beta m \frac{v_x^2}{2}\right) dv_x}{\int_{-\infty}^{\infty} \exp\left(-\beta m \frac{v_x^2}{2}\right) dv_x} + v_y \text{ TERMS} + v_z \text{ TERMS} \right]$$

SINCE v_x, v_y, v_z ARE INDEPENDENT AND EACH OF THE THREE TERMS HAS THE SAME FORM WE CAN WRITE.

$$U = \frac{3}{2} m N \frac{\int_{-\infty}^{\infty} v^2 \exp\left(-\beta m \frac{v^2}{2}\right) dv}{\int_{-\infty}^{\infty} \exp\left(-\beta m \frac{v^2}{2}\right) dv} = \frac{3}{2} m N \left[\frac{\frac{1}{2} \sqrt{8\pi/\beta^3 m^3}}{\sqrt{2\pi/\beta m}} \right]$$

$$\therefore U = \frac{3}{2} \frac{N}{\beta}$$

THE EXPRESSION OF AVERAGE KINETIC ENERGY BECOMES

$$\bar{U} = \frac{U}{N} = \frac{3}{2\beta}$$

FROM KINETIC THEORY OF GASES WE HAVE

$$\bar{U} = \frac{3}{2} KT$$

$$\therefore \frac{3}{2\beta} = \frac{3}{2} KT$$

$$\boxed{\beta = \frac{1}{KT}}$$

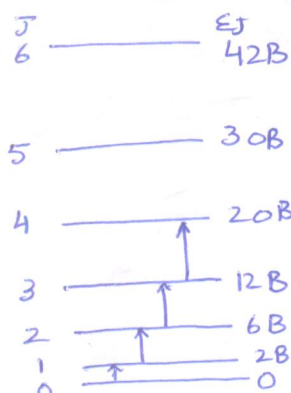
★ EQUATIONS AND STEPS UNDERLINED IN RED ARE ESSENTIAL ALONG WITH

LONG ANSWER TYPE QUESTIONS
CONTINUED

Q6. WHAT ARE SELECTION RULES? GIVE THE SELECTION RULES FOR THE FOLLOWING:

- a) RIGID ROTOR DIATOMIC MOLECULE
- b) RIGID ROTOR-HARMONIC OSCILLATOR MODEL

ANS 6 CONSIDERING THE ENERGY LEVEL DIAGRAM FOR A RIGID DIATOMIC MOLECULE.



WE NEED TO CONSIDER DIFFERENCES BETWEEN LEVELS IN ORDER TO DISCUSS THE SPECTRUM, i.e. A STEPWISE RAISING OF THE ROTATIONAL ENERGY RESULTS IN AN ABSORPTION SPECTRUM CONSISTING OF LINES AT $2B, 4B, 6B, \dots \text{cm}^{-1}$

IN DERIVING THIS PATTERN WE HAVE MADE THE ASSUMPTION THAT A TRANSITION CAN OCCUR FROM A PARTICULAR LEVEL ONLY TO ITS IMMEDIATE NEIGHBOUR. SUCH THAT ALL OTHER TRANSITIONS BEING SPECTROSCOPICALLY FORBIDDEN. SUCH A RESULT IS CALLED A SELECTION RULE

- a) FOR A RIGID ROTOR DIATOMIC MOLECULE
SELECTION RULE $\Delta J = \pm 1$
 - b) FOR A RIGID ROTOR-HARMONIC OSCILLATOR MODEL
 $\Delta v = \pm 1, \pm 2, \text{etc.}$ $\Delta J = \pm 1$
- WHERE v = VIBRATIONAL QUANTUM NUMBER
 J = ROTATIONAL QUANTUM NUMBER

★ DESCRIPTION OF THE VARIABLES ESSENTIAL.

SECTION B

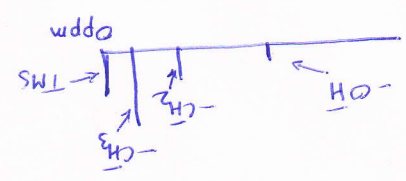
LONG ANSWER TYPE QUESTIONS
CONTINUED

1. FOR THE GIVEN ORGANIC COMPOUNDS IDENTIFY THE DIFFERENT TYPES OF NUCLEI. COMMENT ON THEIR CHEMICAL SHIFT WITH RESPECT TO TMS. ETHANOL; METHANOL

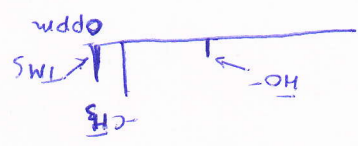
THE DIFFERENT TYPES OF NUCLEI IN ETHANOL - C, O, H OUT OF WHICH ^1H , ^{13}C ARE NMR ACTIVE. IN METHANOL C, O, H OUT OF WHICH ^1H , ^{13}C ARE NMR ACTIVE.

THE DIFFERENCE IN NMR FOR ^1H IN A GIVEN MOLECULE ARISES DUE TO THE DIFFERENCE IN THEIR CHEMICAL ENVIRONMENT. \rightarrow ONE CAN IDENTIFY HYDROGEN IN THREE DIFFERENT CHEMICAL ENVIRONMENTS PROTON ATTACHED TO AN ELECTRONEGATIVE ATOM EXPERIENCES DESHIELDING THEREFORE IS AWAY FROM TMS (THE SIGNAL IS AWAY FROM TMS IN THE DOWNFIELD REGION)

SIMILARLY CH_2 PROTONS ARE DESHIELDED MORE THAN CH_3 PROTONS IN AN SPECTRUM THE SIGNALS CAN BE REPRESENTED IN THE FOLLOWING ORDER



SIMILARLY THE METHANOL SIGNAL CAN BE REPRESENTED AS FOLLOWS



SECTION B

LONG ANSWER TYPE QUESTIONS

CONTINUED

8 EXPLAIN THE FOLLOWING TERMS MULTIPLE SPIN-SPIN SPLITTING, PULSE.

(WITH REFERENCE TO NMR SPECTROSCOPY).

NMR SPECTROSCOPY ARISES FROM THE FACT THAT NUCLEI HAVE A PROPERTY KNOWN AS SPIN. ($I \neq 0$) ONCE PLACED IN AN EXTERNAL MAGNETIC FIELD THE ENERGY LEVELS SPLIT INTO TWO (FOR $I = \frac{1}{2}$).

SIMILAR TO THE ADDING FIGURE CONSIDER A TWO SPIN STATE.

A SPECTRUM OF TWO COUPLED SPINS CONSISTS OF TWO DOUBLETS EACH SPLIT BY THE SAME AMOUNT, ONE CENTERED AT THE CHEMICAL SHIFT OF THE FIRST SPIN AND ONE AT THE SHIFT OF THE SECOND. AS GIVEN IN FIG. 2.

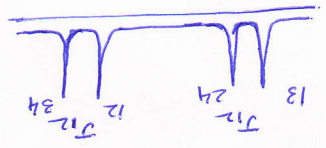
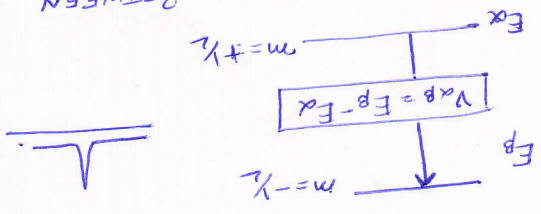


FIG. 2. SCHEMATIC SPECTRUM OF TWO COUPLED SPINS SHOWING DOUBLETS WITH EQUAL SPLITTING

FIG. 1. THE TRANSITION BETWEEN THE TWO ENERGY LEVELS OF A SPIN-HALF IS ALLOWED.



ALLOWABLE TRANSITIONS

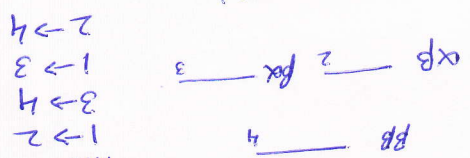


FIG. 3. REPRESENTATION OF ENERGY LEVELS FOR TWO SPIN SYSTEM.

THE ABOVE SET OF DIAGRAMS HIGHLIGHT THE SPIN-SPIN SPLITTING OBSERVED FOR A COUPLED SPINS.

PULSE IN TERMS OF AN NMR IS TERMED AS THE APPLICATION OF A RADIOFREQUENCY TO FLIP THE NET MAGNETIZATION OF ALL PRECESSING NUCLEI TO ALLOW FOR THEIR DETECTION. SINCE THE RELAXATION ARE DIFFERENT THE DURATION OF DIFFERENT CHEMICAL ENVIRONMENT ARE DIFFERENT FOR DETECTION AND INTENSITY OF THE PULSE WHEN MANIPULATED ALLOWS FOR DETECTION OF DIFFERENT (HYDROGEN NUCLEI).