CHEMEN GMA

Instructions
(Prelims Round)
29 June 2021

1. The duration of the exam is 5 hours. However, an additional time of 1 hours might be taken without incurring any penalty. This net duration of 6 hours is **inclusive** of any unforeseen delays in scanning and uploading. The **hard** deadline is set at **6 PM IST, 10th July 2022**. Any submission after that will not be considered. Only one submission per team will be allowed.

2. We highly encourage you to start the process of submitting your answers in the Google form (see below) by 5:00 PM IST. Late submissions, in any case, will not be accepted. If you face persisting network issues during submission, inform us immediately by email (**chemenigma.pravega@gmail.com**) or call Dev at **+91 7990545501**.

3. This paper contains 15 questions in total, including 5 short answer questions and 10 long answer questions. There are **29 pages** in this question paper.

4. Mention question number and title (which is given at the beginning of each question) clearly. We advise writing the question number at the middle of the page to avoid it being cut out during scanning. Answer all subparts of a

1

question together and begin each question in new page. Clearly mention the subpart number for each question.

5. Clearly write your name(s), the name of your institute, as well as your registered email ids at the beginning of the answer script.

6. Do not submit multiple documents. If you have both typed and handwritten answers, compile your documents as a **single** pdf or word file.

7. It is preferred that you name the file as "Participant 1 Full Name_Participant 2 Full Name" (in case of team participation) or "Participant Full Name" (in case of individual participation).

8. Show your steps clearly for both short answer questions and long answer questions. Do not skip steps to receive full credit. Partial credit may be awarded for an incomplete solution or progress towards a solution.

9. In case of any clarification required kindly mail us. We will try our best to clarify. Even after that, if you feel you have any comments regarding the question (for example, incompleteness, incorrectness, etc.) you can mention that in your answer clearly with all the reasons why you think so. If we feel that you claim is correct, scoring will be done accordingly. But the first priority should be getting it clarified from us.

10. You are free to do beyond what is asked to do in the question (though it will not be considered for evaluation). You are also free to add any comments in your answer regarding any question.

11. The exam is open book. You may consult any non-living sources such as books, internet etc but you must cite the sources if you use them. In case you fail to do so, you will be penalised on grounds of plagiarism, and it may even lead to disqualification of the team.

12. If there are any corrections to any question, those will be informed to you over mail.

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Submissions **MUST** be made using the form
https://forms.gle/YA1vBxyBfYLHXqXU7

</div>

Best of Luck!

Questions
260 points

1 (*50 points - 10 points each*) Short Answer Questions

1.1

Mr. Kamal Kumar is an enthusiastic chemist and wants to explore diverse fields connected to chemistry, just like some of you. Chemical Biology is his new fad. He is trying to decode the mystery of proteins and nucleic acids using some ingenious experiments and state-of-the-art tools available to him. Recently, he is focusing on a new compound which he had studied in his advanced biochemistry classes. The compound (A) is nothing but the dephosphorylated product of 3-hydroxy-2-oxopropyl phosphate in an alkaline medium.

(a) Give the IUPAC name of the compound (A) and propose a suitable mechanism for obtaining A from 3-hydroxy-2-oxopropyl phosphate

(*1 points*)

(b) Deduce all the possible isomers for the compound (A).

(*2 points*)

(c) Mr. Kamal tried to study its reactivity with several classes of compounds. One of his experiments focused on reacting compound (A) with a compound containing mercaptan as the functional group while another contained a nitrogenous analogue of carbonic acid. Which of these will react faster with (A), under physiological conditions? Explain your reasoning

(*2 points*)

(d) Now, he reacted compound (A), under physiological conditions, with an amino acid having a guanidine group to form a product (B) and another amino acid containing a thiol group to form a product (C). Predict the products with a plausible mechanism.

(*2+1 points*)

(e) Predict, again with mechanism, the product formed when compound (A) reacts with a dipeptide containing both a thiol and a guanidine group

(*2 points*)

1.2

Have you ever wondered about how test tubes become warm or cold after certain chemical reactions?

The change in temperature occurs due to the enthalpy change in a particular reaction. A negative change in enthalpy means heat will be released and the temperature of the system increases while a positive change in enthalpy means heat will be absorbed from the surroundings and thus the system will cool.

Our aim in a chemical reaction is to analyze how temperature varies. Let us look at a particular recation :

$$A + H_2O \longrightarrow B$$

where A and B are substances with $(C_p)_1$ and $(C_p)_2$ which are temperature invariant constants. C_p of water is $(C_p)_w$ and again temperature invariant.

The $\Delta H°$ is the standard enthalpy of this reaction.

The $\Delta S°$ of the reaction does not vary with temperature. C_v is also same for both substances and also for water. Reaction occurs under isobaric and isochoric conditions.

Water is present in excess and assume nth order kinetics of this recation. Assume Arrhenius equation holds true as well.
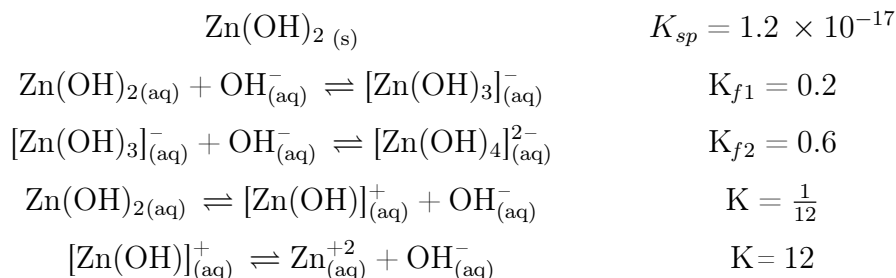
$$k = Ae^{(E/RT)}$$

Find **Temperature as a function of time** (just writing the correct differential equation is enough)
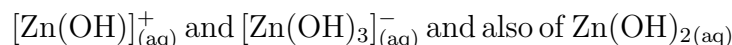
(10 points)

1.3

It is well-known that zinc is an amphoteric metal and its solubility has interested researchers around the world. Based on the information given below, answer the questions that follow:

$$Zn(OH)_{2\,(s)} \qquad\qquad K_{sp} = 1.2 \times 10^{-17}$$

$$Zn(OH)_{2(aq)} + OH^-_{(aq)} \rightleftharpoons [Zn(OH)_3]^-_{(aq)} \qquad K_{f1} = 0.2$$

$$[Zn(OH)_3]^-_{(aq)} + OH^-_{(aq)} \rightleftharpoons [Zn(OH)_4]^{2-}_{(aq)} \qquad K_{f2} = 0.6$$

$$Zn(OH)_{2(aq)} \rightleftharpoons [Zn(OH)]^+_{(aq)} + OH^-_{(aq)} \qquad K = \tfrac{1}{12}$$

$$[Zn(OH)]^+_{(aq)} \rightleftharpoons Zn^{+2}_{(aq)} + OH^-_{(aq)} \qquad K = 12$$

Neglect the concentration of

$$[Zn(OH)]^+_{(aq)} \text{ and } [Zn(OH)_3]^-_{(aq)} \text{ and also of } Zn(OH)_{2(aq)}$$

Find :-

(a) pH of minimum solubility of $Zn(OH)_2$ (aq)

(*3 points*)

(b) Solubility vs pH graph of $Zn(OH)_2$ (aq)

(*3 points*)

(c) Find the pH as a function of solubility

(*4 points*)

1.4

The Wittig reaction is one of the most important reactions in organic chemistry, holding the immense potential to convert a carbonyl group to an alkene group. A ylide generated from a phosphonium salt is necessary for the reaction to take place. Predict the products of the following reaction sequence along with mechanism:

(*10 points*)
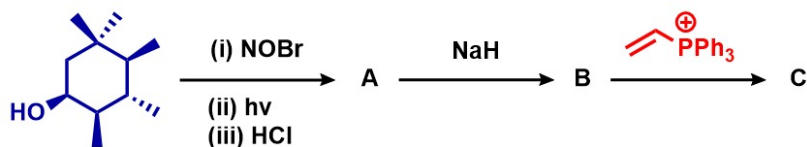
1.5

You are doing your summer project in Dr. Kani Tsaro's lab. He works on studying the kinetics of organic reactions by running a reaction while constantly taking IR readings of the reaction mixture so that he ends up with absorbance as a function of time and wavenumber. Today he started off with a flask of 0.1M methyl ketone in an acidic medium of 60 wt% H_2SO_4. Due to a scheduled power cut, the machine stops working midway, so he loses the data. However, he has to present his work tomorrow, so he asks you to model the reaction and reproduce the IR features.

(a) Identify the reaction.

(*1 points*)

(b) Write a detailed mechanism for the above reaction.

(*1 points*)

(c) Identify the peaks that appear in the IR spectrum during the reaction.

(1 points)

(d) Using your answers for the above questions, model the heights of the peaks as a function of time, assign variables to any parameters that you deem fit; and report your answers in absorbance as a function of time and those variables.

(4 points)

(e) Qualitatively plot the heights of the different IR peaks identified in part (c) as a function of time.

(3 points)

NOTE: You may neglect all peaks in the fingerprint region.

2 (*210 points*) Long Answer Questions

2.1   (*20 points*) Azide - the Amide Bond Builder

Amides are amongst the most fundamental functional groups being present in proteins. Several methods have been developed to form amide bonds easily. Let us delve into the use of azides as possible "amide formers".

2.1.1

Suppose we react cyclohexanone with alkyl azides, it was observed that the reaction is very unfavorable and doesn't give us the amide. However, if the azide was present in the cyclohexanone moiety, then an intramolecular reaction was favourable. Provide the reasoning for the observation. How would you increase the reactivity of the ketone for the reaction to proceed in the forward direction?

(*2 points*)

2.1.2
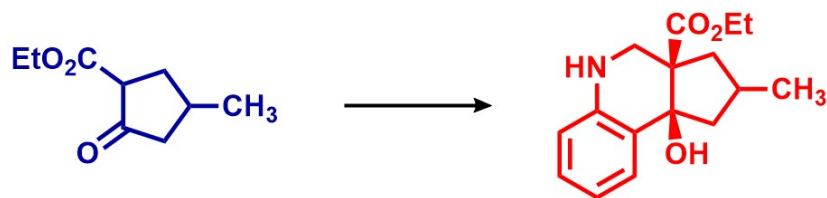
For performing the above reaction, the following reagents are provided.

  (a) $TfOH/CH_2Cl_2$

  (b) $TiCl_4/CH_2Cl_2$

  (c) $PhCH_2N_3$

Propose two mechanisms by which the conversion can be made. (*7 points*)

2.1.3

A scientist was interested in finding the product he would obtain on reacting 4-(azidomethyl)aniline with acetone (in excess) in the presence of a strong acid such as triflic acid taken in catalytic amounts. He obtained two products and conducted an IR analysis of the compounds. The IR spectrum of Product (A) was as the scientist expected but he was surprised at the IR spectrum of Product (B) as it had a peak missing around 3300 cm^{-1}. Decipher the products obtained.

(*3 points*)

2.1.4

Starting with 4-bromo butanoic acid, obtain the corresponding azido-aldehyde in no more than 4 steps. Write down all the steps. On reacting the S-form of the azido aldehyde with an acid, only one product is obtained. Draw the structure of the final product and explain why other product(s) is not obtained.
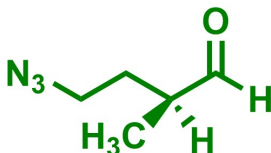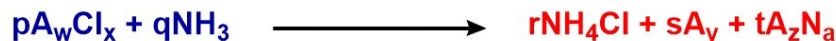

(8 points)

2.2 *(30 points)* Mystery compound

A golden colored binary molecule "X" is the most important compound of its kind, having the capability to form innumerable compounds. Here, we delve into learning more about this mystery compound.

2.2.1

"X can be prepared by a variety of methods, mostly employing the elemental chloride. When the elemental chloride is passed through a solution of ammonia or ammonium chloride, "X" is generally formed.

(a) Consider the reaction of the elemental chloride (405.108 g) with ammonia (136.248 g), ammonium chloride (320.95 g) is generated along with two co-products. One of them being our molecule of interest (92.144 g) and another, an element (128.26 g). Figure out the element of interest "A" according to the equation below with appropriate calculations.

$$pA_wCl_x + qNH_3 \longrightarrow rNH_4Cl + sA_y + tA_zN_a$$

(5 points)

8

(b) Consider the reaction with ammonium chloride, the side products along with "X" are an acid and the element formed in (a). However, in this reaction, the yield was low (∼25%). Upon reaction, it was observed that a purple-brown colored solid was obtained. Propose the possible reason why this color was observed rather than the golden color expected and guess why the yield might be so low?

(2 points)

2.2.2

(a) It is generally believed that "X" has a cradle-like structure. However, for the sake of curiosity, assume it has a planar shape. Assume that the open circles denote that the positive and negative lobe of the p-orbital face the reader and the black circles denote that they face away from the reader. Arrange the following MO's in a qualitative energy diagram.
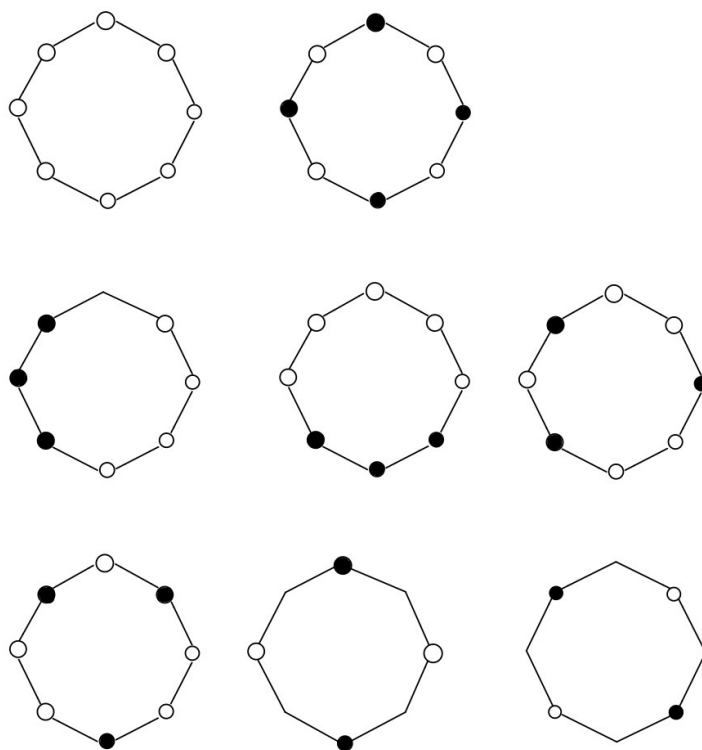
(2 points)

(b) The cradle structure forces one of the two elements to be planar while the other element is out of plane. Now, that you qualitatively arranged the atomic orbital configurations. Predict why does "X" adopt a cradle-like structure and deduce how it might do that?

Helpful information on bond distances of A:

Bonding configuration	206 pm
In "X"	258 pm
Non-bonding configuration	325 pm

(3 points)

(c) Predict the structure of the Phosphorus and Arsenic analogue using the figure given below,
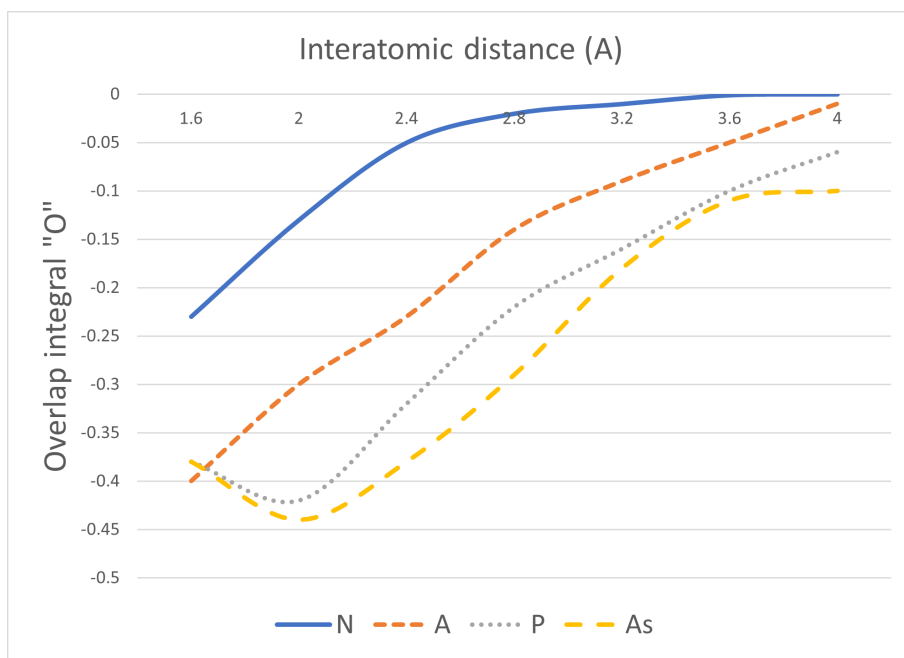
orbital overlap integral "O" vs interatomic distance

Hint: The relative values of "O" for different pairs of atoms at interatomic distance of ≈ 2.4 (why?) are to be considered.

(3 points)

2.2.3

Vaska's complex is a versatile compound capable of undergoing oxidative addition and is well-known to bind to oxygen reversibly. Assume that "X" is capable of binding

to Vaska's complex. It is discovered that the denticity of the ligand "X" is 3. Deduce what changes "X" (in terms of bond lengths) undergoes to coordinate to iridium, if any. Also, Write the balanced reaction of the addition.
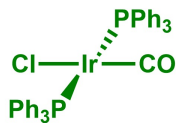

Vaska's Complex

Bonus: Predict the CO stretching frequency as compared to free CO and draw the structure of the adduct formed.
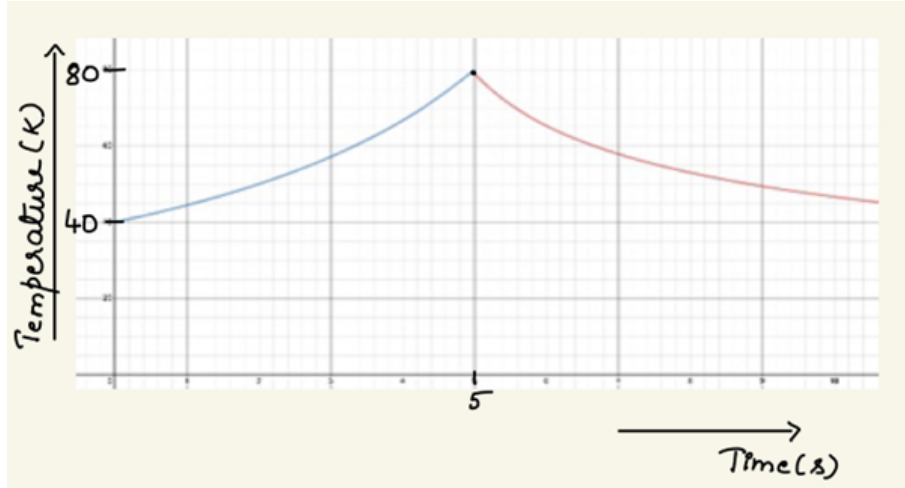
(5 points)

2.2.4

It is noticed that 'X' under controlled conditions can polymerise and gives rise to a polymer that exhibits metallic thermal and electrical properties. In particular, it shows metallic conductivity and attains superconductivity at low temperatures. You set up the following experiment to determine the conductivity of the polymer as a function of its temperature.
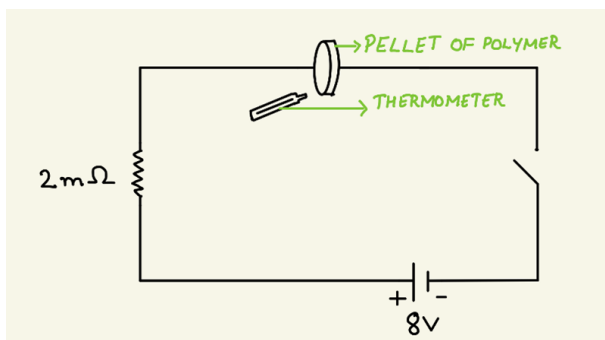
You take the readings in a 40K low temperature chamber, with the pellet initially at 40K. It quickly heats up to 80K in 5 seconds so you switch the circuit off and wait for it to cool down again.

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(a) The time dependance of temperature for the first 5 seconds is 1/(1-t). What is the temperature dependance of the resistivity of the polymer?

(3 points)

(b) What would you expect the time dependance of temperature to be after switching off the circuit?

(3 points)

(c) How long would you expect the pellet to take to cool down to 60K. Pellet thickness is 1mm and radius is 1cm.
(Assign, if necessary, variables to any other parameters and report the answer in terms of those variables.)

(4 points)

2.3   *(15 points)* Fatty acid degradation

Depleting resources, global warming, and climate change. The problems that are associated with fossil fuels are aplenty. Thus, a need to look for alternate "Green fuels" is of prime importance. Bacteria are capable of synthesizing hydrocarbons through fatty-acid derived mechanisms. These hydrocarbon-based biofuels can be a suitable replacement for fossil fuels.

2.3.1

Enzyme "X" is found to be able to catalyze the conversion of fatty acids having a certain chain length into hydrocarbons. X is a family of fatty acid decarboxylases that are present in a certain family of bacterial species. A scientist is interested in knowing if there is a metal present as a co-factor in the enzyme. Bacteria can

convert the inactive "A" form of the enzyme to the active "B" form by an intracellular process. Now, the scientist having the "B" form breaks apart the protein and added a ligand "Y" to characterize the possible metals. He has the absorption spectra of a couple of elements as a reference. He finds that on adding the ligand to the enzyme in the presence of air, the solution appears to be yellowish in nature.

(a) Deduce the metal and its oxidation state present in the enzyme.

(*3 points*)

(b) What might the intracellular process that bacteria utilize?

(*2 points*)
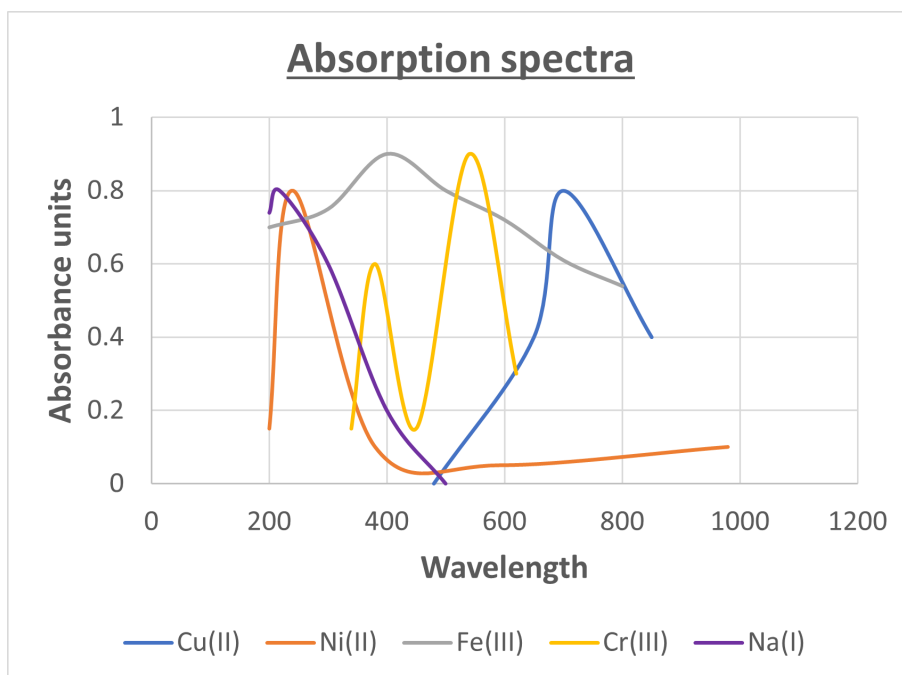
2.3.2

On observing the crystal structure of "X" in the "A" form, the scientist concludes that there is a mononuclear metal "M" center at the active site. As a confirmatory test, he ran a titration between sodium dithionite $Na_2 S_2 O_4$ and 1 mole of "X". The result of the test is as follows:
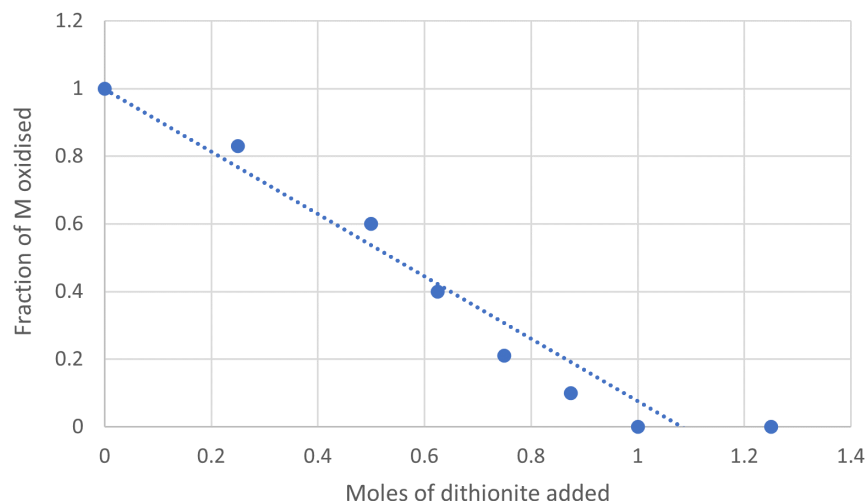
Deduce from the above test if the scientist was correct about his initial conclusion with reason.

(3 points)

2.3.3

The coordination sphere of the metal present in the enzyme in the inactive resting state of the enzyme is usually composed of amino acids and water or oxygen. The scientist subjected the enzyme to irradiation by X-rays and discovered that the adjacent metal distance in "A" is surprisingly small, in units of Angstroms. Upon transversion point mutation of an amino acid, he surprisingly finds that the distance between adjacent iron centers increased. Propose a valid structure of "A", consider all ligands with no importance to the structure to be denoted by X.

(5 points)

2.3.4

The scientist now satisfied with the characterization of the enzyme in the inactive and active states decides to decipher the mechanism of degradation of the fatty acids by "X". He took 3 different substrates and provided them to the enzyme. The substrates were as follows:
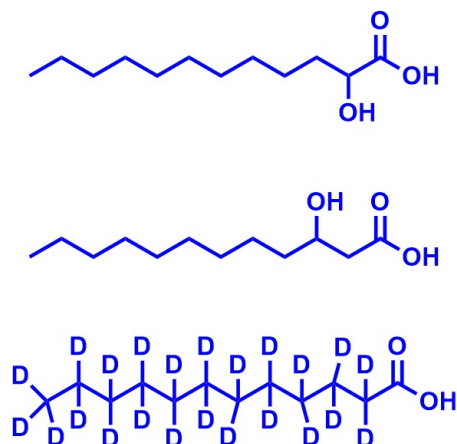
After some time of reaction, the scientist sends the suspected products to an NMR facility. The results he obtained were as follows:

Substrate 1	Form's hydrocarbon (alkene)
Substrate 2	Doesn't form alkene
Substrate 3	Form's hydrocarbon (alkene)

What do you think is a plausible explanation for this observation?

(2 points)

2.4 *(15 points)* Pacman

Mr. Vinod is a great businessman who owns a pizza restaurant in Bangalore. However, being a lazy person he usually changes his socks once a week instead of changing it daily. This lead him to an infectious skin disease athlete's foot. On consulting a doctor he was prescribed to use an antifungal medication[(E)-isomer], the synthesis of the molecule is done as shown below:
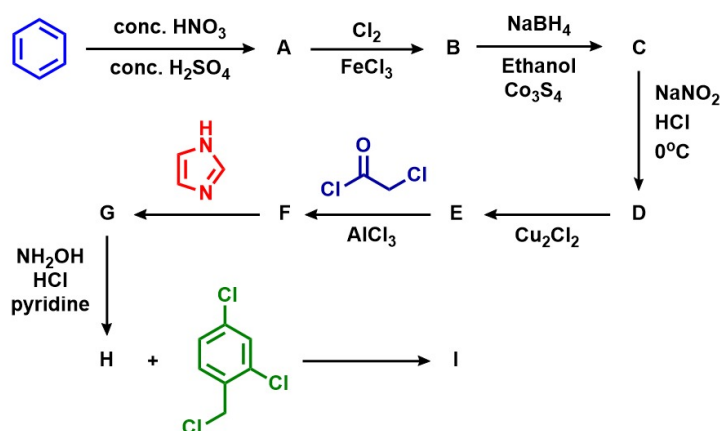
What will be the product formed when the compound I is reacted with an acid, explain with mechanism. Will the product be changed if (Z) isomer of the compound I is reacted instead, explain with mechanism why/why not.

15   (*15 points*)

2.5   *(50 points)* Tongs? Claws?

Researchers are interested in discovering the complexes that some metals make with some fascinating ligands. One particular ligand is J. The reaction scheme is as follows:
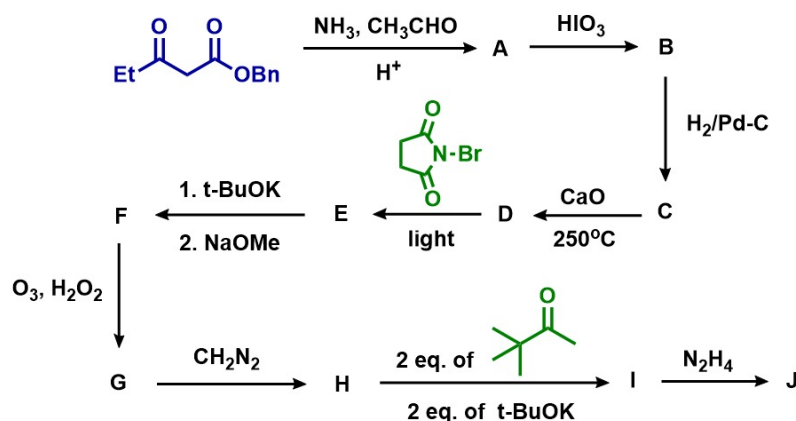
2.5.1

Give the structure of A-J. Note that the conversion to A from the starting material involves an intermediate "K" having a peak at approximately 1700 cm^{-1} and no peak

is observed at 3300 cm^{-1}.

2.5.2
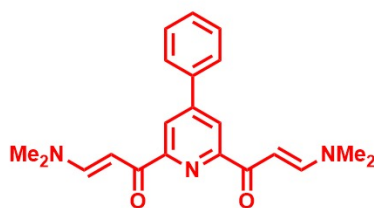
What do you possibly think is the role of HIO_3 and $H_2/Pd-C$ in the above synthesis scheme?

2.5.3

Another ligand similar to I is as follows:

Upon reaction of the above ligand with 2 equivalents of phenyl hydrazine, three isomers are obtained which have different metal binding properties. Draw all the isomers and propose which isomer acts as a tridentate ligand towards metals.

2.5.4

"M" is a versatile element forming a variety of organometallic compounds. The following scheme is an indicator of the variety of the reactions M undergoes. The reagents may or may not be depicted stoichiometrically.
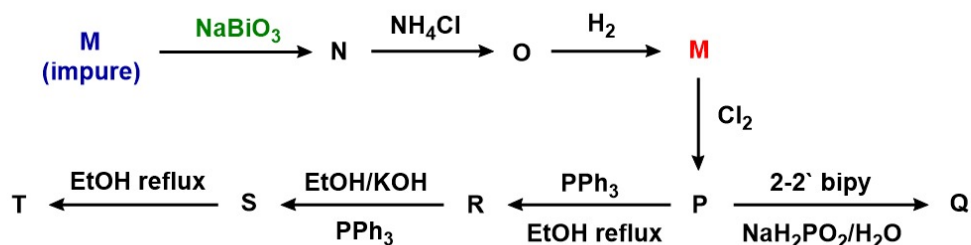
Additional information:

- P is 48.735% of M by mass.

- Q, R, S and T are in the same oxidation state.

- N is a volatile compound.

Based on the above information, answer the following,

(a) Give the structures of N-T. Only give the chemical formula if the complex is non-molecular.
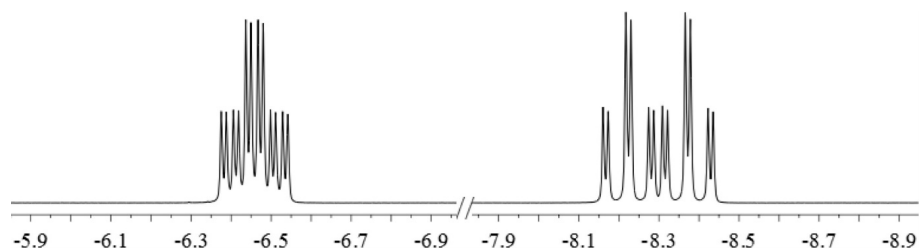
(4 points)

(b) Suppose P $\rightarrow$ R is a reduction reaction, we are interested in finding the reducing agent. After the reaction is complete, the mother liquor is subjected to a decoupled ^{31}P NMR analysis and it is found out that two peaks are formed, one peak on either side of zero. Give a suitable explanation for this observation.

(2 points)

(c) Write all the possible stereoisomers of T. On performing the ^{1}H NMR of T, it was discovered that the both the hydrides appear at negative chemical shifts and display complex coupling patterns. The coupling maybe due to ^{1}H$-$M$-^{31}$P or ^{1}H$-$M$-^1$H. Noting that the coupling constant is greater for trans than for cis.

- What is the signal at -6.8 ppm and at -8.8 ppm?

- Supposing that T is in the mer-cis configuration, assign the coupling constants to each pair of nuclei. The following table will give you an assortment of coupling constants from which you can choose.
(Make sure to label the nuclei; a messy job will earn no points)
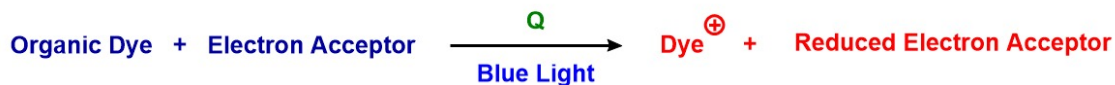
| 31 Hz | 6 Hz | 15 Hz | 74 Hz | 28 Hz |

(10 points)

(d) R on reaction with our ligand J gives a cationic octahedral complex, K (contains one chlorine atom). K upon reaction with half an equivalent of potassium carbonate in the presence of methanol gives L. Give the structures of both K and L.

(5 points)

(e) Q is an interesting molecule, and it acts as a catalyst for the following reaction. Propose a suitable mechanism for the reaction.

Organic Dye + Electron Acceptor $\xrightarrow[\text{Blue Light}]{\text{Q}}$ Dye$^{\oplus}$ + Reduced Electron Acceptor

(*5 points*)

(f) Consider the reaction of P with the molecule generated by the following reaction, give the structure of U and mechanism:

$\xrightarrow{\text{Heat, NaH}}$ U

To determine the stoichiometry of the resulting complex, U. Take 830 mg of "P" in a 500mL flask and made into a series of solutions having total concentration (P+ ligand) 6.24 mM. The following table depicts the volumes taken from the stock into a 1mL tube.

Required volume of stock solution of P to dilute (in microlitre)	Absorbance
250	0.66
252.5	0.71
260	0.83
228.75	0.58
192.5	0.50
161.25	0.41
135	0.33
115.75	0.25

Based on the table, give the composition of the resulting complex.

(4 points)

(g) The complex U thus obtained, following one electron oxidation, is observed to undergo disproportionation. Predict the products of this disproportionation.
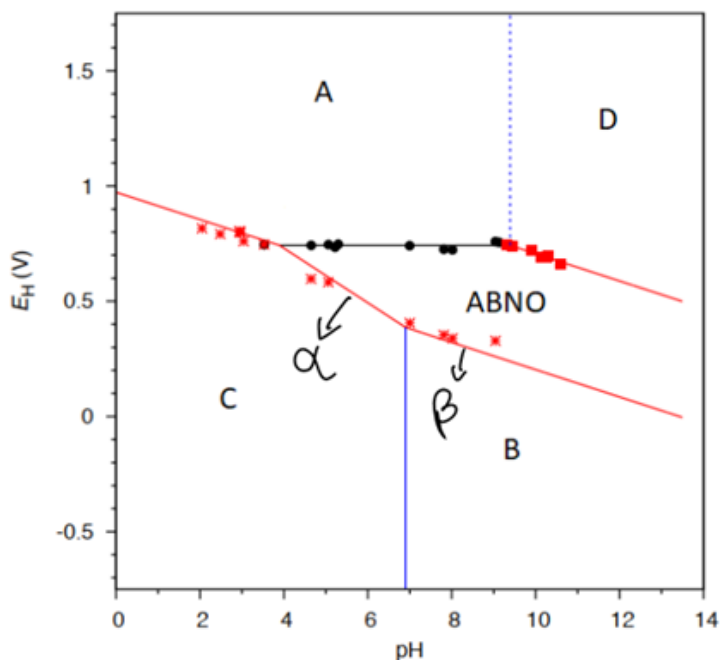
(2 points)

2.6 *(15 points)* ABNO

ABNO is a persistent radical i.e., unlike most other radicals, it is stable and can be isolated and stored for a long time.

9-Azabicyclo[3.3.1]nonane N-Oxyl (ABNO)

The stability of different redox species at specific potential and pH can be represented on a 2 dimensional plot as shown here for the ABNO system. Such a plot is known as Pourbaix diagram. In this diagram, the regions between the lines represent conditions at which one particular species is thermodynamically more stable than all other species. The lines represent equilibrium between two species (in this case at equal concentrations) under standard condition (T = 298.15 K).

Answer the following questions:

(a) A is formed from ABNO by a single electron oxidation and B is formed from ABNO by a single electron reduction followed by protonation. Draw the structures of A, B and C.

(2 points)

(b) Find the ratio of slopes of lines α and β.

(3 points)

(c) An aqueous solution of ABNO is taken to a pH 2. Write the reaction that takes place. What type of reaction is it?

(3 points)

(d) Find the equilibrium constant for the above reaction.

(3 points)

(e) A can be used to oxidise alcohols to aldehydes and ketones in an aqueous medium. In the process A is reduced to B. A is regenerated from B electrochemically. The whole reaction is carried out in an electrochemical cell. Write the reactions taking place in the two electrodes.

(4 points)

2.7   (20 points) An interesting synthesis

You are an emerging young scientist and are passionate about Synthetic Organic Chemistry. One fine day, you decide to do the following reactions. The questions
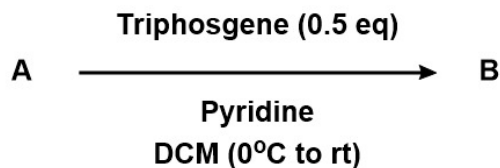
that follow are a series of queries one of the interns in your lab decided to bother you with.

2.7.1
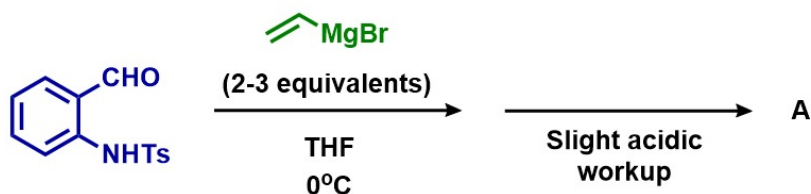
(a) What is A?

(*1 points*)

(b) Why are 2-3 equivalents of Grignard reagent used here?

(*1 points*)

2.7.2

(a) What is the expected product B given that the molecular formula of B is $C_{17}O_4SH_{14}$

(*2 points*)

(b) Propose a mechanism for the above conversion.

(*3 points*)

(c) Why do we need only 0.5 equivalents of triphosgene? Also what is the role of pyridine here?
Hint: Think towards the group leaving the triphosgene molecule

(*3 points*)

2.7.3

The Crabbe reaction involves the formation of allenes from alkynes in the presence of a secondary amine and in the presence of copper.
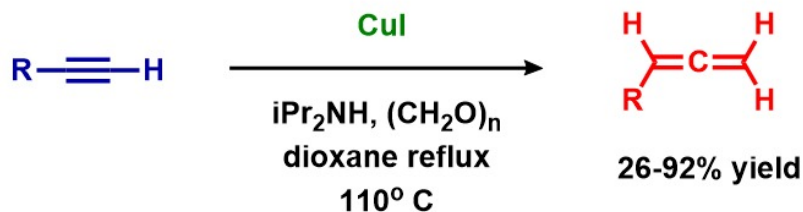
(a) On reaction of Cu^+ with alkynes, the terminal hydrogen becomes more acidic and is capable of being immediately extracted by the iPr_2NH. Explain this observation qualitatively by using coordination chemistry ?

(2 points)

(b) What would be your expected product when the following substrate is used?
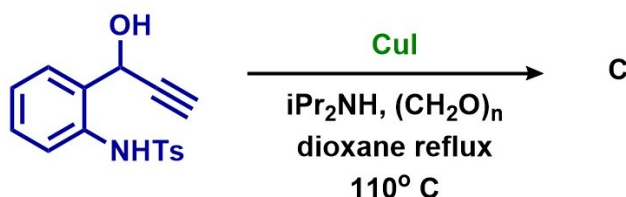
(1 points)

(c) However, upon performing the reaction, you were surprised to see no allene being formed. You send a sample of your product for a ^1H NMR analysis and that confirmed that you do not have an allene as your product. However, cyclised products were formed. Come up with a suitable mechanism that predict the formation of the obtained products.
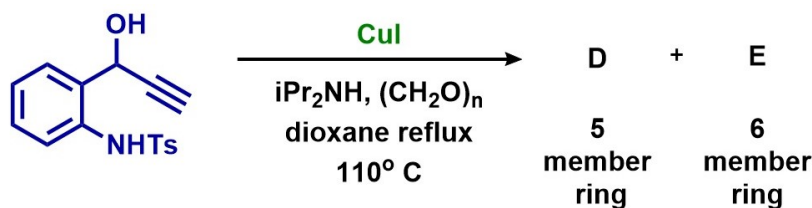
(4 points)

(d) Using Baldwin's rules, what is the theoretically expected product if allene isn't formed?
i) Only D will form
ii) Only E will form
iii) D and E will form in equal amounts
iv) Cannot predict

(1 points)

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(e) Experimentally, it was found out that only the 5-membered ring product was formed. Propose a hypothesis as to why this was observed.
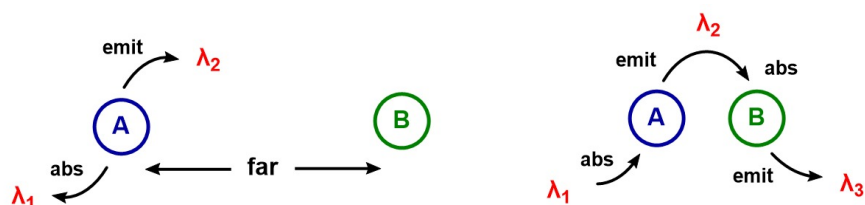
(2 points)

## 2.8 *(15 points)* Electron Transfer Mechanisms

2.8.1

Quenching is a process by which the fluorescence intensity gets reduced by a variety of mechanisms. Some of the mechanisms include Forster resonance energy transfer and dexter electron transfer. The below diagrams give you a flavour of the above mentioned mechanisms. Refer to them and answer the questions that follow.
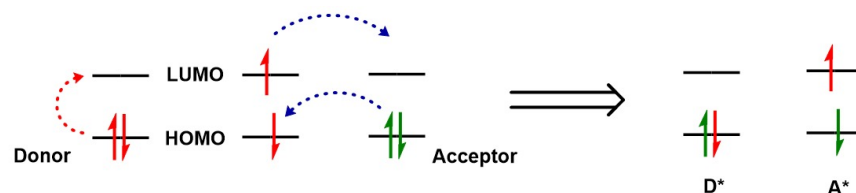

Dexter electron transfer

FRET
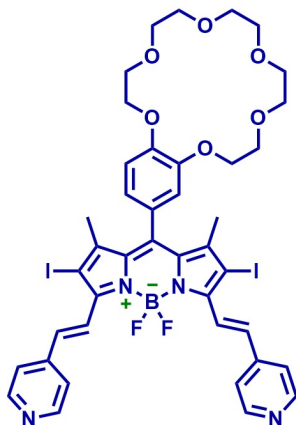
In acidic medium, in presence of a particular ion the above molecule acts as a photosensitizer.

(a) Identify the ion and the type of logic gate

(*1 points*)

(b) What would be the gate type if the this ion is replaced by the ion of the same group?

(*1 point*)

2.8.2

Under conditions of neutral pH, energy is transferred between the photosensitizer and the fluorophore. The colour emitted is the same as that of the $\lambda_{emission}$ of the fluorophore. In acidic medium, the emitted colour is that of the photosensitizer
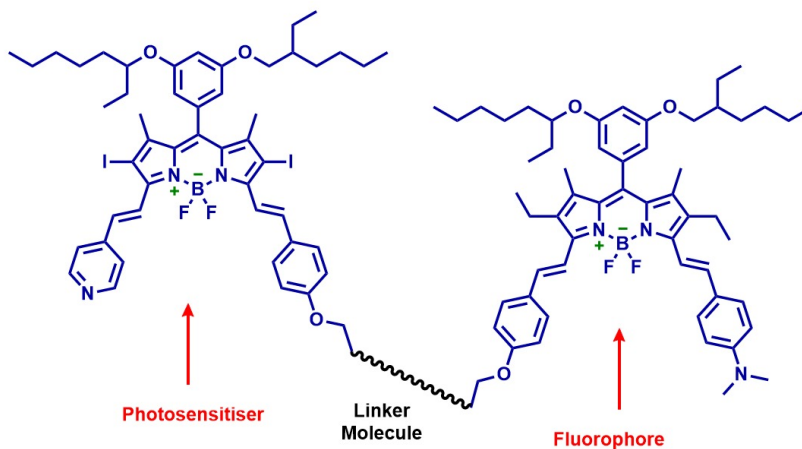
(a) What are the changes in an acidic medium that result in the $\lambda_{emission}$ of the photosensitizer being seen rather than the fluorophore (Give a detailed

explanation)?

(3 points)

(b) Propose a gate logic for the above observation. You are free to use standard gates such as AND, NOR.

Input	Output
$[H^+]$	$\lambda_{emission}$ of photosensor (λ_{ps}^e)
$\lambda_{absorption}$ of photosensor (λ_{ps}^a)	$\lambda_{emission}$ of fluorophore (λ_{fl}^e)

(2 points)

2.8.3

Consider the following molecule. It is structurally very similar to the molecule drawn in Part 2.8.2. It has a fluorophore and a photosensitizer molecule with a linker.
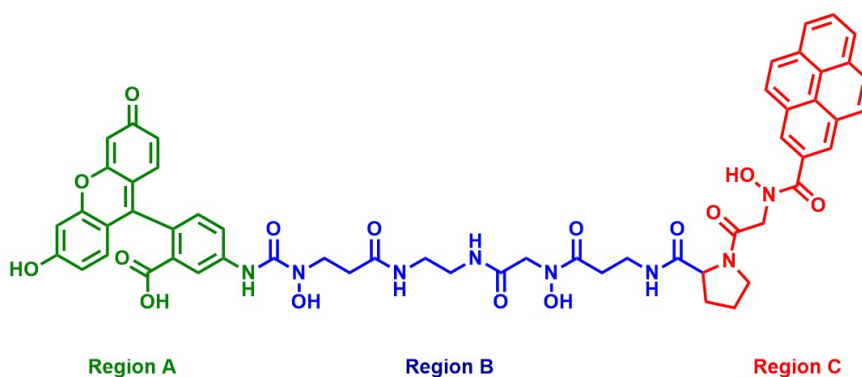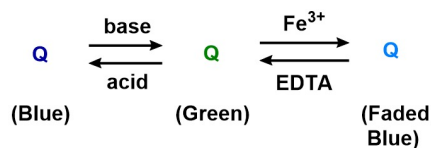

(a) Identify the part of the molecule which acts as the photosensor and which acts as the fluorophore among the following options.

i) Region A
ii) Region B
iii) Region C
iv) Either region A or region B can act as one

(1 point)

(b) Upon performing several experiments, the following schematic is observed in the molecule. Explain the schematic.

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(c) What do you expect would occur if the $-NH-C=O$ links are increased by 6. What colour would you expect when UV light is shone on the molecule after it is subjected to the addition of an acid?

(d) Design two logic boxes with H^+, OH^-, λ_{UV} as input for one box and Fe^{3+}, EDTA, λ_{UV}, the inputs for the second box, and λ_{blue}, λ_{green} as output.

2.9 *(15 points)* **Hamiltonian**

The many electron problem is one of the most fascinating problems of quantum chemistry. It has a rich history, starting from early days of quantum mechanics and continuing to the present day with new intellectual challenges. Consider the Schrodinger's equation (in atomic units, $m_e = e = \hbar = 4\pi\epsilon = 1$) pertaining to the multi-electron system

$$\left(\sum_{i=1}^{n}\left(-\frac{1}{2}\nabla_i^2 + v_{ext}(r_i)\right) + \frac{1}{2}\sum_{i \neq j}\frac{1}{r_{ij}}\right)\psi = E\psi$$

Although this equation can be solved numerically using Monte-Carlo techniques (for smaller values of n), no exact solution exists for this equation. One approach to solve this problem is to construct an approximate wavefunction and optimize it to minimize the expectation value of the Hamiltonian.

$$\frac{\psi_{approx}|H|\psi_{approx}}{\psi_{approx}|\psi_{approx}} \geq E_{ground}$$

2.9.1

Suppose, we consider electrons to be moving independently in an average nuclear potential v_{ext}. Show that the expectation energy of the n-electron system is given by

$$E = \sum_{i=1}^{n}\phi_i| - \frac{1}{2}\nabla^2|\phi_i + \int v_{ext}(r)\rho(r)dr + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr' - \frac{1}{2}\sum_{i=1}^{n}\iint \frac{|\phi_i(r)|^2\,|\phi_i(r')|^2}{|r-r'|}drdr'$$

where $\phi_i(r_i)$ are wavefunctions of individual electrons and $\rho(r)$ is the total electron density at position r

Hint :

(a) Since the electrons are assumed to move independently in an average field, the wavefunction of the system would simply be the product of individual wavefunctions i.e,

$$\psi(r_1, r_2, ..., r_n) = \phi_1(r_1)\phi_2(r_2)....\phi_n(r_n)$$

where $\phi_i(r_i)$ are wavefunctions of individual electrons.

(b) The total electron density $\rho(r)$ at a position r is the sum of individual electron densities at position r, i.e,

$$\rho(r) = \sum_{i=1}^{n} \int \phi_i^*(r)\phi_i(r)dr$$

(*10 points*)

2.9.2

Consider the simplest multi-particle system - Two Particles in 1-D Box. Plot the distribution $(|\psi(r)|^2$ vs $r)$ that will be obtained using the approach described above and compare it with the expected distribution.

(*5 points*)

2.10   (*15 points*) Spectroscopy and Green House Effect

We all are aware of Global Warming, the Rise of CO_2 levels, the rise of sea levels, etc. CO_2 is Infra-Red (IR) active as IR radiation is enough to excite bonds of CO_2 i.e., causes stretching C=O bond. Thus, it can trap IR radiation and warms the atmosphere. We cannot have CO_2 free atmosphere, as it is essential for the survival of many florae. So, let us estimate the near-optimum amount of CO_2 in the atmosphere.

Let us consider a very small biome consisting of 1 plant and 130 human beings (quite small, isn't it?). A pine tree can absorb 0.13 tons of CO_2 per day and a human exhales 1.04 kg of CO_2. It is clear that the ratio is not ideal. There will be an accumulation of CO_2 in the biome.

The stretching frequency of the C=O bond is 1715cm-1. Let us consider a mole of CO_2 as a system at room temperature. This system is exposed to IR radiation including the frequency of $1715\,\mathrm{cm}^{-1}$. Let us assume the frequency other than 1715cm-1 is transmitted completely by the system. Answer the following:

(a) How is CO_2 IR active as it has no net dipole moment?

(*1 points*)

(b) What will be the temperature after the prolonged exposure to the IR radiation assuming the system consists of ideal gases?

(3 points)

(c) What will be the temperature if the system consists of 78% N_2, 21% O_2, and 0.03% CO_2 and other IR inactive gases assuming all gases are ideal?

(3 points)

(d) What will change if gases are van-der Waal gases?

(5 points)

(e) What steps can be taken to get the ideal ratio of trees: humans assuming all trees are identical w.r.t. consuming CO_2? You can't kill humans.

(3 points)

3   *(5 points)* *Tie breaker* (Optional, will only be considered in case of a tie)

Oktoberfest has arrived*! It is time for drunken frolicking, raunchy singing and vigorous fist thumping. All round you can see sloshed faces with creamy moustaches screaming "Prost!".

But soon, the air turns macabre as three people from a tent collapse. They are rushed to the nearby hospital. Doctors claim that the collapse is due to cardiomyopathy caused by excess cobalt ions.

Where does cobalt come from and why? (Explain the chemistry of what cobalt does here)