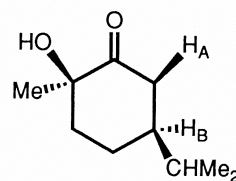


Exam 2: CHEM/BCMB 4190/6190/8189 (133 points) Thursday, 1 October, 2020

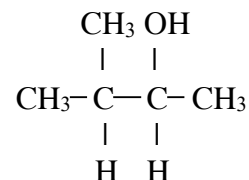
1). For a sample of CHCl_3 , you apply a very long (seconds), low power pulse at the ^1H frequency of the single ^1H nucleus in the molecule. Immediately after this pulse, you apply a normal, high power 90 degree pulse at the same frequency and then record the FID. Sketch what you would expect the FID to look like. Also, sketch the spectrum you would expect to observe following Fourier transformation of the FID. You must thoroughly explain your answers for credit. **(6 points)**.

2). When the cyclohexanone shown (right) is dissolved in methanol, the three-bond scalar coupling constant between H_A and H_B ($^3J_{\text{H}_\text{A}\text{H}_\text{B}}$) is 11 Hz. However, when it is dissolved in benzene, this coupling is 3 Hz. Please explain in detail why the couplings are different and the origins of the difference. For credit, your answer must include the word “Karplus” used in a contextually correct way. **(6 points)**



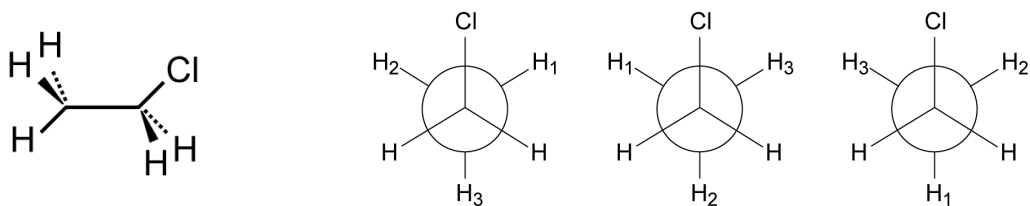
3). Consider the isomerically pure compound (*S*)-(+)-3-methyl-2-butanol (right).

a. Indicate how many signals will be in the ^1H NMR spectrum (ignore the hydroxyl hydrogen). You will have to explain/justify your answer for credit. **(4 points)**



b. State what the multiplicity is for each signal (i.e. doublet, triplet, triplet of doublets, etc.). Then, provide a detailed but concise explanation of your answer. Assume that 4-bond, 5-bond, or longer range couplings are *NOT* observed. Also, assume that there are no observable couplings to the hydroxyl hydrogen. **(15 points)**

4). Consider chemical and magnetic equivalence in ethyl chloride



For each of the following questions, you will need to provide a detailed explanation in order to receive credit!

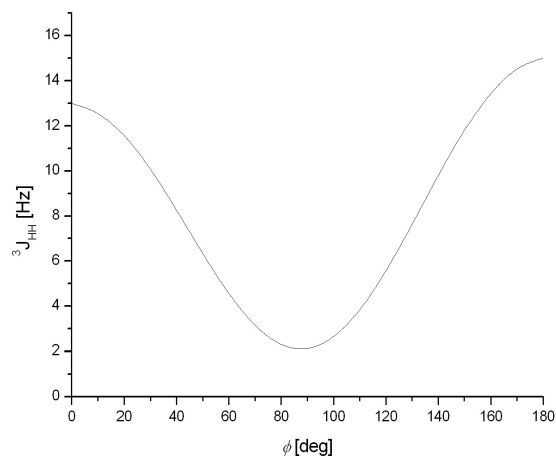
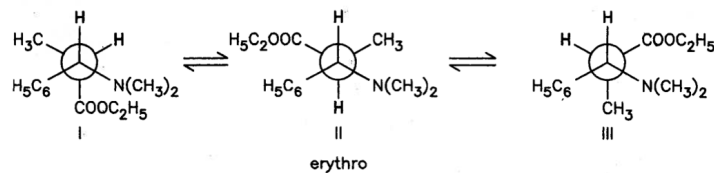
a. Are the two methylene hydrogens chemically equivalent? Why? **(4 points)**

b. Are the three methyl hydrogens chemically equivalent? Why? **(4 points)**

c. Are the methylene hydrogens magnetically equivalent? Why? **(4 points)**

d. Are the methyl hydrogens magnetically equivalent? Why? **(4 points)**

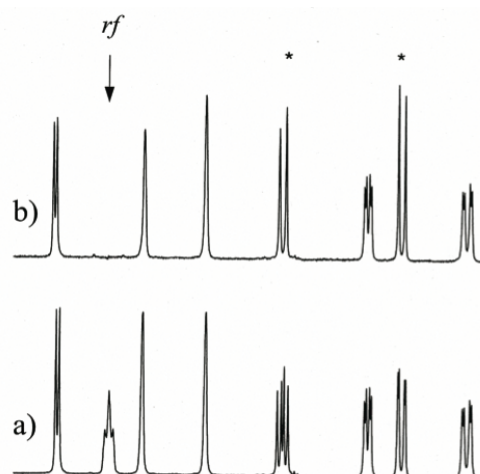
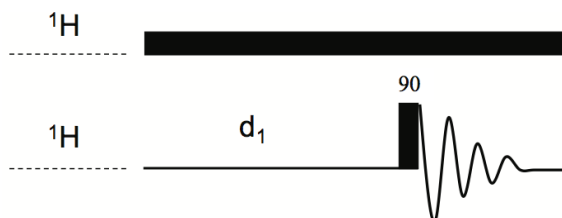
5). The Karplus curve for ethylene derivatives is shown (right). The three rotamers of the *erythro* isomer 2-methyl-3-dimethylamino-3-phenylpropionic acid ethyl ester are shown below.



a. If you measured the magnitude of the 3-bond (vicinal) coupling constant between the two methine hydrogens of 2-methyl-3-dimethylamino-3-phenylpropionic acid ethyl ester, and found it to be equal to 4 Hz ($^3J_{HH} = 4$ Hz), what might you conclude regarding the relative populations of conformers I, II, and III? Please explain. **(4 points)**

b. If you measured the same coupling constant as a function of increasing temperature, and found that the value increased to about 7.5 Hz ($^3J_{HH} = 7.5$ Hz) and then leveled off and did not further increase as the temperature was increased, what would you conclude regarding the relative populations of conformers I, II, and III? Please explain. **(4 points)**

6). For a particular molecule, the homonuclear (^1H - ^1H) selective decoupling experiment was performed using the pulse sequence diagrammed below, with the results shown (right), where the result in 'a' is without decoupling, and the result in 'b' is with decoupling. In 'b', the arrow indicated by "rf" points the frequency at which the decoupling field is applied.

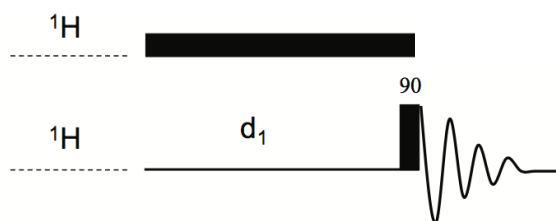


a. In general, for a pair of coupled hydrogens in a molecule, explain the mechanism by which application of a long pulse at the Larmor frequency of one of them leads to decoupling and loss of splitting in NMR spectra? Please use complete sentences and no diagrams or equations. (4 points)

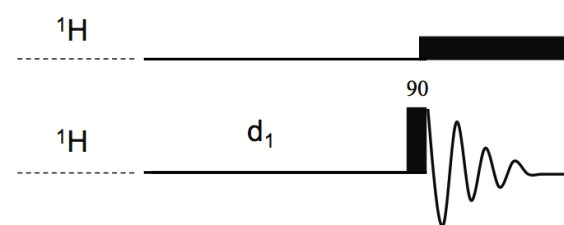
b. Explain why the decoupling experiment (pulse sequence) shown above results in the spectra shown in 'b'. Your explanation should address all changes to signals in 'b' compared to 'a' and the mechanisms by which these result from using the decoupling pulse sequence. (4 points)

Name _____

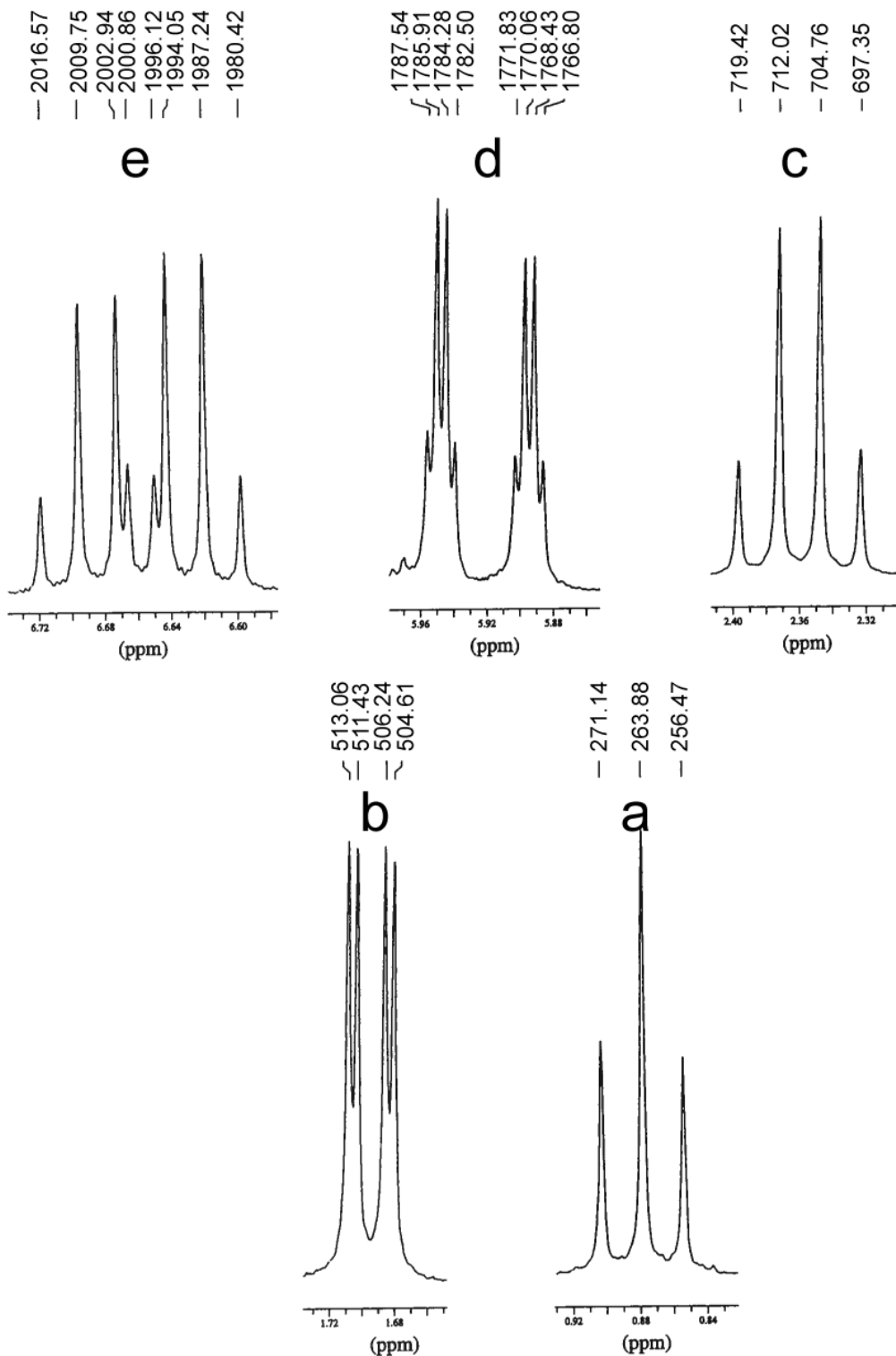
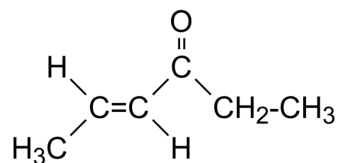
c. Describe the result you would expect to observe if, instead of using the pulse sequence shown above, the experiment was performed with the pulse sequence shown here (right). You will have to explain or otherwise justify your answer for credit. **(4 points)**



d. Describe the result you would expect to observe if, instead of using the pulse sequence shown above, the experiment was performed with the pulse sequence shown here (right). You will have to explain or otherwise justify your answer for credit. **(4 points)**

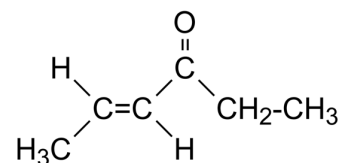


7). The signals from the ^1H NMR spectrum of *trans*-4-hexen-3-one (right) are shown below. The frequencies of the individual peaks in the signals are indicated (in Hz).



a. Calculate the field strength (in Tesla) of the magnet used to acquire these spectra? (6 points)

b. Label the hydrogens on the molecule (right) a-e, corresponding to the signals shown above. Below, justify each assignment. Your justifications should include explanations as to why the chemical shift, signal splitting, and coupling constant information available in the spectra support your assignments. Coupling constants should be reported using standard nomenclature. (20 points)



Signal a.

Signal b.

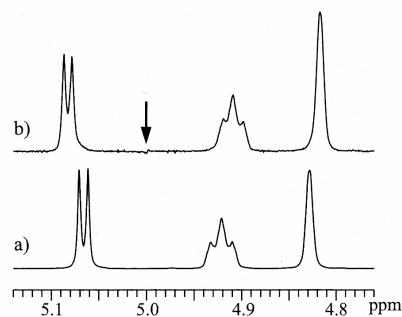
Name _____

Signal c.

Signal d.

Signal e.

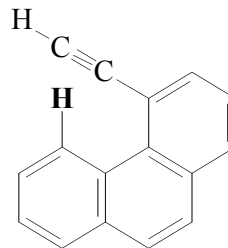
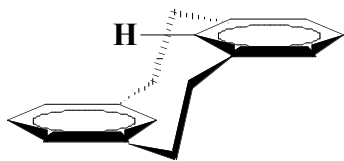
8). When performing selective homonuclear decoupling experiments, if the decoupling field is applied during the acquisition of the FID, signals in the spectrum ('b') can move relative to their positions in the control spectrum ('a') where no decoupling field is applied. This is demonstrated in the spectra shown (right), where the arrow indicates the frequency at which the decoupling field was applied for spectrum 'b'. This effect is known as the Bloch-Siegert effect. This effect is not observed if the decoupling field is turned off prior to acquisition. Provide a plausible explanation for the Bloch-Siegert effect. (8 points)



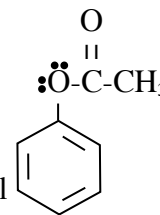
9). Circle the word in each pair of parentheses that makes the following statement true: As the value for the shielding constant, σ , increases, this indicates (decreased / increased) shielding of a nucleus, a/an (decrease / increase) in the effective magnetic field experienced by the nucleus, a/an (downfield / upfield) shift in the chemical shift, and a (lower / higher) resonance frequency for the nucleus. (4 points)

10). Why is the term σ_{para} necessary to describe the shielding constant, σ ? (4 points)

11). For benzene, the ^1H chemical shift of the hydrogens is 7.27 ppm. For ethane, ethylene, and acetylene, the ^1H chemical shifts of the hydrogens are 1.96, 5.84, and 2.88 ppm, respectively. Estimate the chemical shift of the shown (bolded) hydrogen atom in each of the two molecules shown below. You will need to thoroughly explain and justify your answers. (6 points)



12). The ^1H and ^{13}C NMR spectra of phenyl ethanoate (right) were recorded. The ^1H signals for the protons in the benzene ring (ignoring coupling) were, from largest to smallest, found to be 7.25, 7.15, and 7.06 ppm. The ^{13}C signals for the carbon atoms in the benzene ring (ignoring coupling) were, from largest to smallest and not including the ^{13}C chemical shift of the carbon bound to the oxygen, found to be 128.9, 125.3, and 121.4. You also know that for unsubstituted benzene, the chemical shift of the protons is 7.27 ppm and the chemical shift of the ^{13}C atoms is 128.5 ppm.



- a. Indicate in the table below which of the ^1H and ^{13}C shifts correspond to the ortho, meta, and para positions by placing the correct chemical shift in the correct position in the table. (6 points)

	Chemical Shifts		
	δ_{ortho}	δ_{meta}	δ_{para}
^1H			
^{13}C			

- b. Justify your answer to part 'a'. In order to receive credit for parts 'a' and 'b' you will have to 1). draw appropriate resonance structures to justify your table entries, and 2). discuss why each position is more/less shielded relative to the others. (8 points)

Name _____

THIS PAGE IS BLANK. FEEL FREE TO USE IT AS “SCRATCH” IF YOU LIKE

You may find some of the information below useful:

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment ^{a)} [eQ] [10^{-28} m^2]	Natural abundance) [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio $\gamma^a)$ [$10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488 \text{ T}$)
^1H	1/2	–	99.985	1.00	26.7519	100.0
^2H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
$^3\text{H}^c)$	1/2	–	–	1.21	28.5350	106.664
^6Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04×10^{-3}	-2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
^{19}F	1/2	–	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84×10^{-3}	-5.3190	19.865
^{31}P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	–	8.58	5.18×10^{-2}	-10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

B_0 (Tesla, T)	Resonance frequencies (MHz)	
	^1H	^{13}C
9.4	400	100.6
11.74	500	125.7
14.09	600	150.9
18.79	800	201.2

$$\gamma_{^1\text{H}} = 26.7519 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{10}\text{B}} = 2.8747 \times 10^7 \text{ rad/T/s}, I = 3$$

$$\gamma_{^{11}\text{B}} = 8.5847 \times 10^7 \text{ rad/T/s}, I = 3/2$$

$$\gamma_{^{13}\text{C}} = 6.7283 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{15}\text{N}} = -2.7126 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{17}\text{O}} = -3.6280 \times 10^7 \text{ rad/T/s}, I = 5/2$$

You may find some of the following information or equations useful:

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$\text{Avagadro's number} = 6.02214179 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\hbar = h/(2\pi)$$

$$P = \hbar \sqrt{I(I+1)}$$

$$P_z = m\hbar$$

$$\mu = \gamma P = \hbar \gamma \sqrt{I(I+1)}$$

$$\text{for } m = \frac{1}{2}, \cos(\theta) = \frac{m\hbar}{\hbar \sqrt{I(I+1)}} = \frac{m}{\sqrt{I(I+1)}}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$$

$$B_2 = \frac{\Delta \nu \sqrt{J^2 - J_r^2}}{J_r} = \frac{J \Delta \nu}{J_r}$$

$$\varepsilon \propto dM/dt = \gamma M_0 B = \frac{N\gamma^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}$$

$$\Delta \nu = \nu_{BS} - \nu_0 = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(\nu_0 - \nu_i)}$$

$$S/N \propto NS^{1/2} \text{ (signal-to-noise improves with (number of scans)}^{1/2})$$

$$m = (-I, -I+1, \dots, I-1, I)$$

$$\Theta = \gamma B_1 \tau_p$$

$$E = -\mu_z B_0 = -m\gamma \hbar B_0$$

$$\frac{N_\beta}{N_\alpha} \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T} \right)$$

$$\Delta E = \mu_z B_0 = \gamma \hbar B_0 = h\nu_L = h\nu_1$$

$$B_{eff} = B_0(1 - \sigma)$$

$$\nu_L = |\gamma/(2\pi)| B_0 = \omega_0/(2\pi)$$

$$\nu_L = \frac{\gamma}{2\pi} (1 - \sigma) B_0$$

$$\omega_0 = \gamma B_0$$

$$\Delta \delta = \frac{\Delta \nu}{\text{observe frequency}} \times 10^6$$

$$M_y = M_0 e^{-t/T_2^*}$$

$$M_z = M_0(1 - e^{-t/T_1})$$

$$M_z = M_0(1 - 2e^{-t/T_1})$$

$$\Delta \nu_{1/2} = \frac{1}{\pi T_2^*}$$

$$\frac{1}{T_2^*} = \frac{\gamma \Delta B_0}{2} + \frac{1}{T_2} \quad \frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2(B_0)}$$

$$t_{\text{zero}} = T_1 \ln(2)$$

$$\eta = \gamma_a / (2\gamma_x)$$

$$I = (1 + \eta) I_0$$

$$I \propto 1/r^6$$

$$SW = 1/(2DW) = \text{Nyquist frequency } (\nu_{NQ})/2$$

$$AQ = DW * TD$$

$$DR = 2SW/TD = 1/AQ$$

$$(TD \equiv NP)$$

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$1 + \gamma_A/\gamma_X \quad 1 - \gamma_A/\gamma_X$$

$$\text{multiplicity} = 2nI + 1$$

$$\Theta = 2\pi J \tau$$