NMR problems 3rd part

1. Due to elements of symmetry within the structure of the molecule, the $^{13}$C NMR spectrum of ethane contains only a single resonance, the corresponding spectra of $(\text{CH}_3)_2\text{CHBr}$ and $(\text{CH}_3)_3\text{CBr}$ would contain 2 resonances. How many distinct resonances are there in:

1. The $^1\text{H}$ NMR spectrum of $(\text{CH}_3)_4\text{C}$?
2. The $^{13}\text{C}$ NMR spectrum of $(\text{CH}_3)_4\text{C}$?
3. The $^{31}\text{P}$ NMR spectrum of $(\text{CH}_3\text{CH}_2)_3\text{PO}$?
4. The $^{13}\text{C}$ NMR spectrum of $(\text{CH}_3\text{CH}_2)_3\text{PO}$?
5. The $^1\text{H}$ NMR spectrum of $(\text{CH}_3\text{CH}_2)_3\text{PO}$?
6. The $^{29}\text{Si}$ NMR spectrum of $(\text{CH}_3)_3\text{SiSi(\text{Et})}_3$?
7. The $^1\text{H}$ NMR spectrum of $(\text{CH}_3)_3\text{SiSi(\text{Et})}_3$?
8. The $^{13}\text{C}$ NMR spectrum of $(\text{CH}_3)_3\text{SiSi(\text{Et})}_3$?

Answer

This is a very straightforward question once you have correctly written down the 3 dimensional structure of each of the compounds in question. The 3 dimensional geometry and in particular the symmetry associated with each compound allows you to determine which atoms are (or are not) chemically equivalent.

1. $(\text{CH}_3)_4\text{C}$ is a tetrahedral molecule with all 4 methyl groups equivalent. In the $^1\text{H}$ NMR spectrum, there would be 1 NMR signal for the 4 equivalent CH$_3$ groups.

2. $(\text{CH}_3)_4\text{C}$ is a tetrahedral molecule with all 4 methyl groups equivalent. In the $^{13}\text{C}$ NMR spectrum, there would be 1 NMR signal for the 4 equivalent carbons of the methyl groups and one for the quaternary carbon at the centre of the molecule (2 signals in all).

3. There is only one phosphorus in this molecule - there would be only one signal in the $^{31}\text{P}$ NMR spectrum.

4. The bonding in $(\text{CH}_3\text{CH}_2)_3\text{PO}$ is tetrahedral at phosphorus. Each ethyl group has 2 non-equivalent C atoms, but the 3 ethyl groups are equivalent. In the $^{13}\text{C}$ NMR spectrum, there would be 1 NMR signal for the CH$_3$ groups and 1 for the CH$_2$ groups (2 signals in all).

5. The 3 ethyl groups are equivalent. In the $^1\text{H}$ NMR spectrum there would be 1 NMR signal (a multiplet) for the protons of the CH$_3$ groups and 1 for the protons of the CH$_2$ groups (2 signals in all).

6. $(\text{CH}_3)_3\text{SiSi(\text{CH}_3\text{CH}_2)_3}$ contains 2 Si atoms - they are non-equivalent since one has 3 methyl substituents and one has 3 ethyl substituents. In the $^{29}\text{Si}$ NMR spectrum there would be 2 signals.

7. The bonding in $(\text{CH}_3)_3\text{SiSi(\text{CH}_3\text{CH}_2)_3}$ is tetrahedral at each of the silicon atoms. All 3 methyl substituents attached to one silicon are equivalent and would give rise to one signal in the $^1\text{H}$ spectrum. All 3 ethyl substituents on the second silicon are equivalent and each would have 1 NMR signal for the CH$_3$ groups and...
1 for the CH₂ groups. So overall there would be 3 signals in the ¹H spectrum.

8. The bonding in (CH₃)₃SiSi(CH₃CH₂)₃ is tetrahedral at each of the silicon atoms. All 3 methyl substituents attached to one silicon are equivalent and would give rise to one signal in the ¹³C NMR spectrum. All 3 ethyl substituents on the second silicon are equivalent and each would have 1 NMR signal for the CH₃ groups and 1 for the CH₂ groups. So overall there would be 3 signals in the ¹³C NMR spectrum.

2. Due to elements of symmetry within the structure of the molecule, the ¹³C NMR spectrum of ethane contains only a single resonance, the corresponding spectra of (CH₃)₂CHBr and (CH₃)₃CBr would contain 2 resonances. How many distinct resonances are there in:
   1. The ¹H NMR spectrum of (CH₃)₄C?
   2. The ¹³C NMR spectrum of (CH₃)₄C?
   3. The ³¹P NMR spectrum of (CH₃CH₂)₃PO?
   4. The ¹³C NMR spectrum of (CH₃CH₂)₃PO?
   5. The ¹H NMR spectrum of (CH₃CH₂)₃PO?
   6. The ²⁹Si NMR spectrum of (CH₃)₂SiSi(Et)₃?
   7. The ¹H NMR spectrum of (CH₃)₂SiSi(Et)₃?
   8. The ¹³C NMR spectrum of (CH₃)₂SiSi(Et)₃?

Answer
This is a very straightforward question once you have correctly written down the 3 dimensional structure of each of the compounds in question. The 3 dimensional geometry and in particular the symmetry associated with each compound allows you to determine which atoms are (or are not) chemically equivalent.

1. (CH₃)₄C is a tetrahedral molecule with all 4 methyl groups equivalent. In the ¹H NMR spectrum, there would be 1 NMR signal for the 4 equivalent CH₃ groups.
2. (CH₃)₄C is a tetrahedral molecule with all 4 methyl groups equivalent. In the ¹³C NMR spectrum, there would be 1 NMR signal for the 4 equivalent carbons of the methyl groups and one for the quaternary carbon at the centre of the molecule (2 signals in all).
3. There is only one phosphorus in this molecule - there would be only one signal in the ³¹P NMR spectrum.
4. The bonding in (CH₃CH₂)₃PO is tetrahedral at phosphorus. Each ethyl group has 2 non equivalent C atoms, but the 3 ethyl groups are equivalent. In the ¹³C NMR spectrum, there would be 1 NMR signal for the CH₃ groups and 1 for the CH₂ groups (2 signals in all).
5. The 3 ethyl groups are equivalent. In the ¹H NMR spectrum there would be 1 NMR signal (a multiplet) for the protons of the CH₃ groups and 1 for the protons of the CH₂ groups (2 signals in all).
6. (CH₃)₂SiSi(CH₃CH₂)₃ contains 2 Si atoms - they are non-equivalent since one has 3 methyl substituents and one has 3 ethyl substituents. In the ²⁹Si NMR spectrum
there would be 2 signals.

7. The bonding in \((\text{CH}_3)_3\text{SiSi(CH}_3\text{CH}_2)_3\) is tetrahedral at each of the silicon atoms. All 3 methyl substituents attached to one silicon are equivalent and would give rise to one signal in the \(^1\text{H}\) spectrum. All 3 ethyl substituents on the second silicon are equivalent and each would have 1 NMR signal for the \(\text{CH}_3\) groups and 1 for the \(\text{CH}_2\) groups. So overall there would be 3 signals in the \(^1\text{H}\) spectrum.

8. The bonding in \((\text{CH}_3)_3\text{SiSi(CH}_3\text{CH}_2)_3\) is tetrahedral at each of the silicon atoms. All 3 methyl substituents attached to one silicon are equivalent and would give rise to one signal in the \(^{13}\text{C}\) NMR spectrum. All 3 ethyl substituents on the second silicon are equivalent and each would have 1 NMR signal for the \(\text{CH}_3\) groups and 1 for the \(\text{CH}_2\) groups. So overall there would be 3 signals in the \(^{13}\text{C}\) NMR spectrum.

3. The chemical shift scale on a NMR spectrum is typically given in dimensionless units termed "parts per million" (ppm) from some reference compound. What is the relationship between a chemical shift scale in Hz. and a scale in "ppm"?

Answer
The resonance frequency of a nucleus (expressed in Hz) is directly proportional to the strength of the applied magnetic field and changes from spectrometer to spectrometer, depending on the strength of the magnet. It is more convenient to express the resonance frequency in dimensionless units (termed "parts per million" or "ppm") by dividing the actual resonance frequency of the nucleus by the Larmor frequency of the type of nucleus being observed. In this way, all chemical shifts are effectively "normalised" to take account of the fact that each different spectrometer may have a different magnetic field strength. Chemical shifts are typically measured relative to the frequency of some standard compound, taken by convention as a reference, and chemical shifts are usually expressed in units of ppm from the resonance of the reference compound. Chemical shifts expressed in ppm are independent of \(B_0\) and are tabulated as characteristic molecular properties. If the Larmor frequency for observing a nucleus in particular spectrometer is 400 MHz then 1 ppm corresponds to 400 Hz.

4. In NMR spectrometers commonly used in medicine, the resonance frequency for the protons in water is 60 MHz. If such an instrument was to be used to observe \(^{31}\text{P}\), what frequency of Rf. radiation would be required?

Answer
The answer to this question requires an understanding of the Larmor equation. One of the things that are obvious from the Larmor equation is that the resonance frequency increases with the magnetogyric ratio. The higher the magnetogyric ratio, the higher the frequency required observing the NMR signal of the nucleus.

The question asks for a comparison between the frequencies required for the observation of protons (\(^1\text{H}\)) and phosphorus (\(^{31}\text{P}\)) in the same magnet. The magnetogyric ratio of \(^{31}\text{P}\) is 0.405 times that of \(^1\text{H}\) so the frequency required to
observe $^{31}$P will be scaled by the same factor:

$^{31}$P frequency = $^1$H frequency x 0.405
= (0.405 x 60) MHz
= 24.3 MHz

5. In a magnetic field of strength 2.349 T, the resonance frequency of $^{15}$N nuclei is 10.13 MHz What is the resonance frequency of $^{15}$N in a magnet of 11.745T?

Answer The answer to this question again requires an understanding of the Larmor equation. From the Larmor equation, the resonance frequency required to observe a certain type of nucleus is proportional to the strength of the magnetic field ($B_0$). The higher the magnetic field, the higher the resonance frequency of a given type of nucleus.

The question asks for a comparison between the frequencies required for the observation of $^{15}$N in two different magnets. The magnetic field strength is increased by a factor of $(11.745/2.349) = 5$ so the frequency required observing $^{15}$N will be scaled by this factor:

$^{15}$N frequency at 11.745T = $^{15}$N frequency at 2.349T x 5
= (10.13 x 5) MHz
= 50.65 MHz

6. The magnetogyric ratio of the deuterium ($^2$H) nucleus is approximately 6.5 times smaller than that of the proton. In a magnet where a $^1$H spectrum can be observed at about 400 MHz, what is the approximate frequency of Rf. radiation you would need to observe the $^2$H NMR spectrum?

Answer The answer to this question is very similar to the answer to Question 4. The question asks for a comparison between the frequencies required for the observation of protons ($^1$H) and deuterium ($^2$H) in the same magnet. The magnetogyric ratio of $^1$H is 6.5 times that of $^2$H, so the frequency required to observe $^2$H will be $1/6.5$ that required to observe $^1$H.

$^2$H frequency = $^1$H frequency / 6.5
= (400 / 6.6) MHz
= 61.54 MHz

7. In a sample of CH$_2$Cl$_2$, the $^{13}$C NMR spectrum is an obvious triplet and the $^1$H NMR spectrum a strong singlet. Rationalize the appearance of the spectra.

Answer The $^{13}$C NMR spectrum of CH$_2$Cl$_2$ has a single resonance for the single carbon in the molecule. The carbon is coupled to 2 equivalent protons so the signal is split to a multiplet of $(2nI + 1)$ lines where $I = \frac{1}{2}$ (for $^1$H) $n = 2$ because there are 2
protons:
\[(2nI + 1) = (2 \times 2 \times \frac{1}{2}) + 1 = 3.\]
The signal will appear as a triplet.

You should ask why the \(^{13}\text{C}\) spectrum exhibits coupling to protons but the \(^1\text{H}\) spectrum does not show coupling to \(^{13}\text{C}\). The answer lies in the low natural abundance of \(^{13}\text{C}\). Only about 1% of all C is \(^{13}\text{C}\) so when you are observing the \(^{13}\text{C}\) you are only observing about 1% of the carbons in the sample. However, the natural abundance of \(^1\text{H}\) is (effectively) 100% so every \(^{13}\text{C}\) you observe will have two NMR-active protons coupled to it. The converse is not true - most \(^1\text{H}\) nuclei will be in molecules where the carbon is not \(^{13}\text{C}\) (since most carbon is \(^{12}\text{C}\) and this is an NMR-silent nucleus).

8. In a sample of \(\text{CH}_2\text{Cl}_2\), the \(^{13}\text{C}\) NMR spectrum is an obvious triplet and the \(^1\text{H}\) NMR spectrum a strong singlet. Rationalize the appearance of the spectra

Answer: The \(^{13}\text{C}\) NMR spectrum of \(\text{CH}_2\text{Cl}_2\) has a single resonance for the single carbon in the molecule. The carbon is coupled to 2 equivalent protons so the signal is split to a multiplet of \((2nI + 1)\) lines where \(I = \frac{1}{2}\) (for \(^1\text{H}\)) \(n = 2\) because there are 2 protons:
\[(2nI + 1) = (2 \times 2 \times \frac{1}{2}) + 1 = 3.\]
The signal will appear as a triplet.

You should ask why the \(^{13}\text{C}\) spectrum exhibits coupling to protons but the \(^1\text{H}\) spectrum does not show coupling to \(^{13}\text{C}\). The answer lies in the low natural abundance of \(^{13}\text{C}\). Only about 1% of all C is \(^{13}\text{C}\) so when you are observing the \(^{13}\text{C}\) you are only observing about 1% of the carbons in the sample. However, the natural abundance of \(^1\text{H}\) is (effectively) 100% so every \(^{13}\text{C}\) you observe will have two NMR-active protons coupled to it. The converse is not true - most \(^1\text{H}\) nuclei will be in molecules where the carbon is not \(^{13}\text{C}\) (since most carbon is \(^{12}\text{C}\) and this is an NMR-silent nucleus).

9. The protons of the 3-chlorobutyrate ion \([\text{CH}_3\text{CHClCH}_2\text{CO}_2^-]\) can be labeled as an \(\text{A}_3\text{MXY}\) spin system.
1. Exactly what information tells you about the spin system?
2. Could the \(^1\text{H}\) NMR spectrum of this molecule be analyzed by normal first-order rules? Why?

Answer
1. The label \(\text{A}_3\text{MXY}\) indicates that:
   (a) There are 6 nuclei in the spin system, and
   (b) The 6 nuclei occur at 4 different shifts with one shift environment having 3 chemically equivalent nuclei and the others having 1 proton; (c) The fact that two of the spins are given the letters X and Y (which are close together in the alphabet) indicates that this part of the spin system has \(\langle J \rangle < 3\).
2. Because one part of the spin system has \(\langle J \rangle < 3\), the spin system is not first order and could not be analyzed using normal first order rules.
10. What would happen to the widths of the $^1$H NMR signal in a sample of CH$_3$Br when:
1. A soluble Fe(III) salt was added to the solution.
2. The solution was scrupulously deoxygenated before the spectrum was acquired.
3. The solution was cooled to near its freezing point.

**Answer**
1. Fe(III) is paramagnetic so a soluble paramagnetic salt in an NMR sample will efficiently relax the nuclei in the sample. Nuclei which relax rapidly give rise to broad signals in the NMR spectrum.
2. Oxygen is paramagnetic and even small amounts of oxygen dissolved in the sample contribute to relaxation. So if the sample was rigorously degassed, this would remove oxygen and the lines would get sharper because the relaxation would be less efficient.
3. When a solution is cooled to near its freezing point, it becomes viscous and less mobile. Solutes dissolved in the solution are less mobile and tumble more slowly as the viscosity is increased. Relaxation is more efficient when molecular motion is slowed so lines become broader as the solution becomes more viscous.

11. An NMR sample contains protons with both relatively short (say 100 ms) and long (say 10 sec) relaxation times. What would be the qualitative appearance of a series of $^1$H NMR spectra of the sample acquired rapidly (say successively at intervals of 4 seconds)?

**Answer** If spectra are acquired in quick succession, the signals from the species with the long relaxation time will not have sufficient time to relax between acquisitions. On the other hand, the species with the short relaxation time would be fully relaxed between acquisitions.

In the first spectrum, the intensity of signals would exactly represent the concentration of species giving rise to them since the nuclei are fully relaxed prior to acquisition. For the second spectrum (4 seconds later) the nuclei with relaxation time 100 ms will be fully relaxed and will give a signal which is identical to the first spectrum. However the nuclei with long T1 will not be fully relaxed by the time the second spectrum is recorded and the signal intensity will therefore be less. The effect is re-enforced in the 3rd, 4th etc spectrum so after many acquisitions, the intensity of the signals from rapidly relaxing nuclei is relatively accurately defined however the signals from slowly relaxing nuclei will be underestimated.

12. What would happen to the T$_1$ values for the protons and widths of the $^1$H NMR signal in a solution of CH$_3$Br when:
1. A soluble Fe(III) salt was added to the solution.
2. The sample was dissolved in a solvent with a substantially higher viscosity, e.g. an oil.
3. The solution was scrupulously deoxygenated before the spectrum was acquired.
4. The solution was cooled to near its freezing point.

Answer
1. Fe(III) is paramagnetic so a soluble paramagnetic salt in an NMR sample will efficiently relax the nuclei in the sample. Addition of a paramagnetic salt will reduce T₁ values and give rise to broad signals in the NMR spectrum.
2. When a solution is cooled to near its freezing point, it becomes viscous and less mobile. Solutes dissolved in the solution are less mobile and tumble more slowly as the viscosity is increased. Relaxation is more efficient, relaxation times are reduced, so lines become broader as the solution becomes more viscous.
3. Oxygen is paramagnetic and even small amounts of oxygen dissolved in the sample contribute to relaxation. So if the sample was rigorously de-oxygenated, relaxation times would increase and the lines would get sharper because the relaxation would be less efficient.
4. Relaxation is more efficient when molecular motion is slowed. Viscous solvents restrict molecular tumbling so relaxation times decrease and the lines become broader as the solution becomes more viscous.

13. The ¹H NMR spectrum of an organic molecule is usually sharp with resonances which have lines < 0.3 Hz wide. A ²H NMR spectrum of the same sample typically has resonances which are significantly broader with lines approximately 1 Hz (or more) in width. Rationalize this difference.

Answer The ²H spectrum is broader because the relaxation times of ²H nuclei are always shorter than for ¹H. This arises because ²H has a spin of 1. Nuclei with spin other than ½ are called quadrupolar nuclei and relaxation in quadrupolar nuclei is dominated by the presence of the quadrupole. Quadrupolar relaxation, for some quadrupolar nuclei, can be so efficient that the NMR spectra are broadened to the extent that they can't be detected.