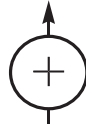


INTRODUCTION TO NUCLEAR MAGNETIC RESONANCE (NMR)

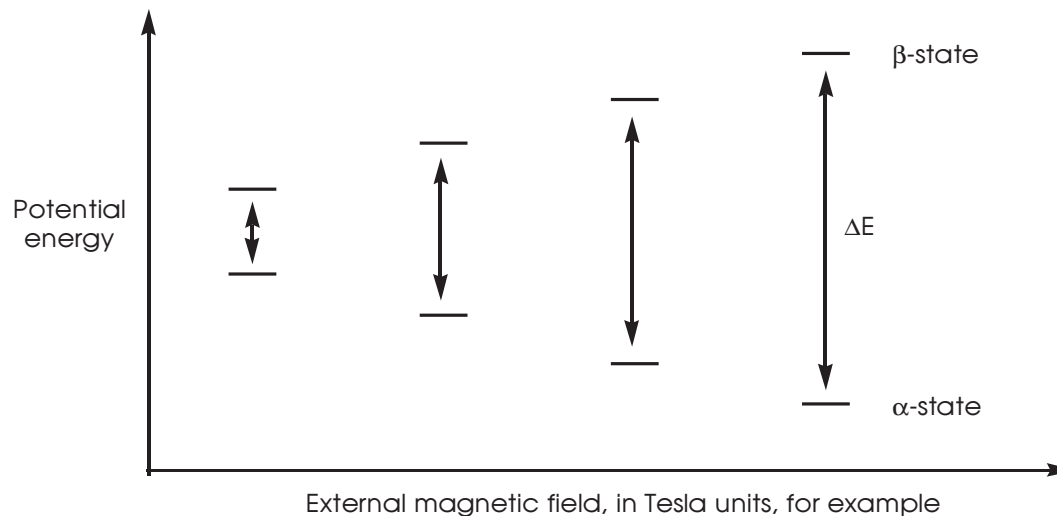
BASIC PRINCIPLES

1. The nuclei of certain atoms with odd atomic number, and/or odd mass behave as spinning charges. The nucleus is the center of positive charge, and this spinning charge generates a tiny magnetic field, indicated as a vector with a magnitude and direction.

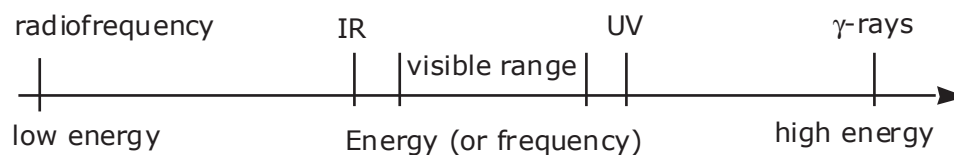


2. If a chemical sample containing such atoms is placed inside a magnetic field (also referred to as external, or applied field), the nuclear magnetic moment can only acquire a finite number of orientations, according to the principles of quantum mechanics. For proton (H-1) and for carbon-13 (C-13) the number of possible orientations is two: aligned with or against the field. When the nucleus is aligned with the field it is said to be in the α -state. When it is aligned against the field it is said to be in the β -state. Such atoms are then referred to as **magnetically active**, and for us later on, also as **NMR active**.

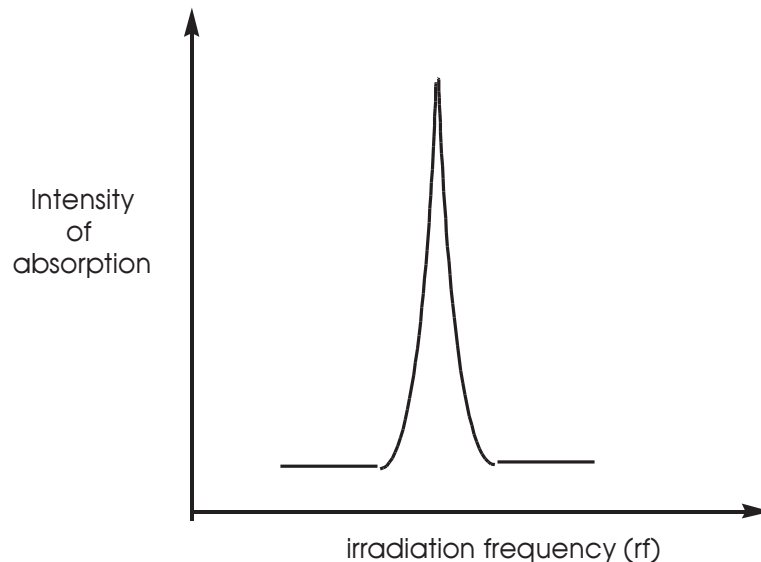
3. The potential energy associated with these two states is not the same. The α -state is of lower potential energy than the β -state. Furthermore, the energy difference (or gap) between the two states increases as the strength (intensity) of the external field increases.



4. It is possible to excite, or “flip” the nuclear magnetic vector from the α -state to the β -state by bridging the energy gap between the two. This is accomplished by irradiating the sample with electromagnetic radiation of the correct frequency (which is proportional to its energy). Such radiation source happens to be in the radiofrequency (rf) region of the electromagnetic spectrum. The energy of this type of radiation is relatively low compared to x-rays, or even visible light, for instance.

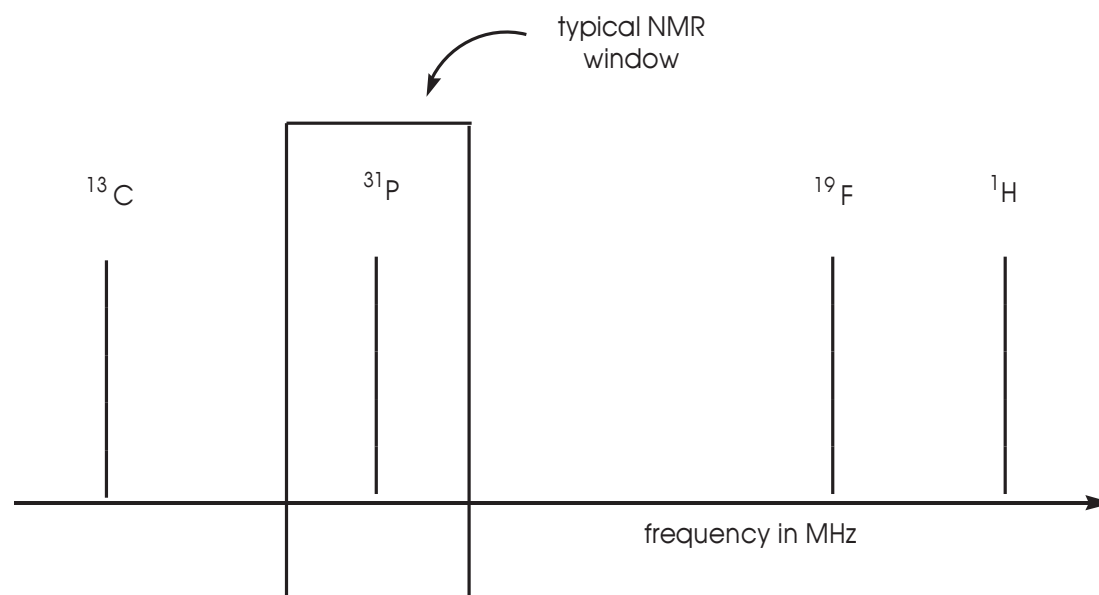


6. When absorption of energy occurs, a radiofrequency signal is induced in a detector coil located in the sample probe (housing). The instrument records this frequency absorption as a resonance signal, or peak.



7. Since ΔE depends on the external magnetic field strength, the signal occurs at different rf values for different magnets.

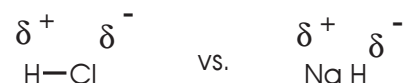
8. The nuclear spin is a nucleus-specific property. Different elements have different absorption ranges. They usually do not interfere with each other unless their absorption ranges are very close, which is rare. For example, at a magnetic field strength of 1 Tesla, the absorption frequency for the H-1 nucleus is approximately 43 MHz (megahertz). At the same field strength, C-13 absorbs at 10.7 MHz, F-19 at 40 MHz, and P-31 at 17.2 MHz. If this frequency range was shown to scale, it would show that the signals for different elements are so far apart that only one nucleus can be observed at a time under the conditions of a typical experiment.



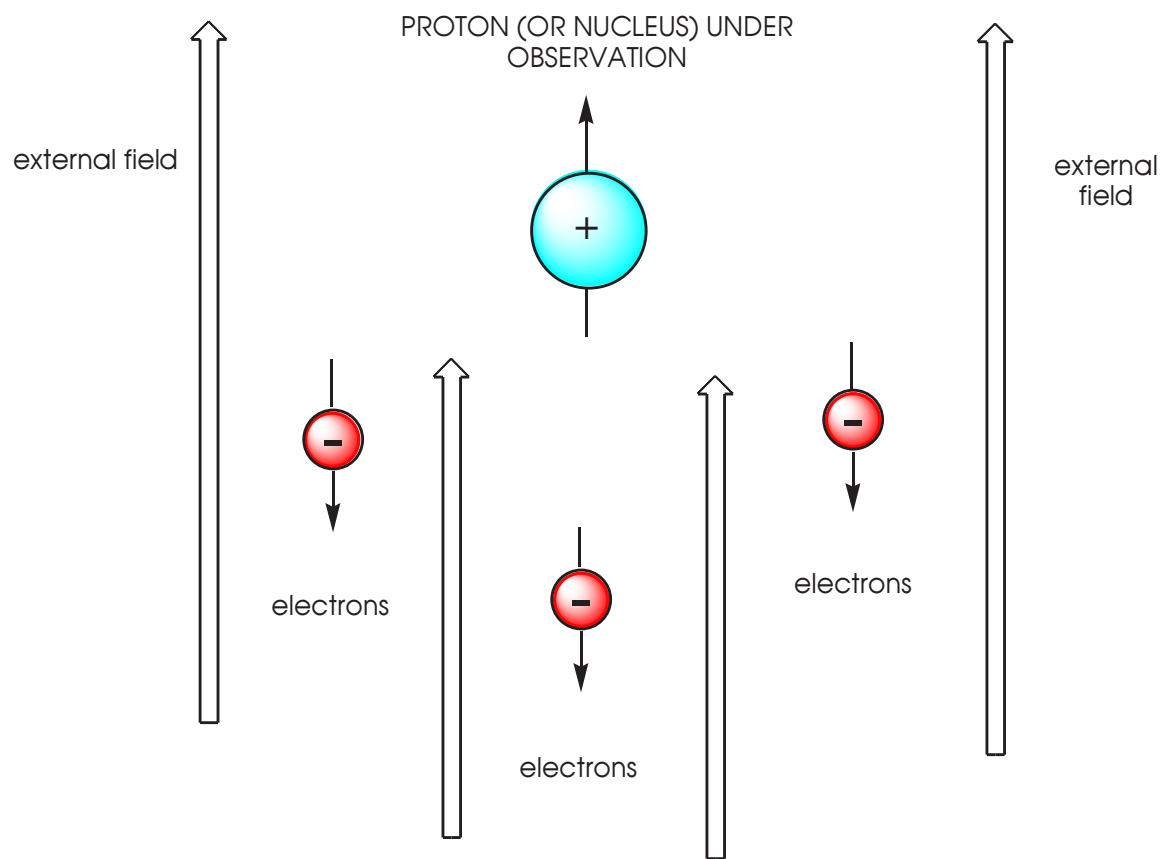
9. The information contained in a common NMR spectrum typically falls into four categories: (a) **number of signals present**, (b) **chemical shift** (position of the signals in the frequency axis), (c) **relative signal intensities**, and (d) **signal multiplicities**.

THE CHEMICAL SHIFT

1. The nucleus under observation is typically a part of a whole molecule. This means that the electron density around different nuclei is not the same. For example "acidic protons" (those bonded to highly electronegative atoms) have less electron density than protons bonded to carbon. Hydrogen bonded to metals (also known as hydride) carries a partial negative charge and therefore has a high degree of electron density:



2. The electrons that surround the nucleus are also magnetically active and they generate their own tiny magnetic vectors. In the presence of an external field these electronic vectors **oppose** the nuclear vector. Therefore the electrons act as tiny shields, protecting the nucleus from the full effect of the external field. The higher the electron density, the more “shielded” the nucleus is from the external field. For example, if we could place HCl and NaH under the same magnetic field, the hydrogen nuclei in these compounds would not experience the field strength to the same extent. The hydrogen in NaH would be more shielded than the hydrogen in HCl due to its higher electron density.



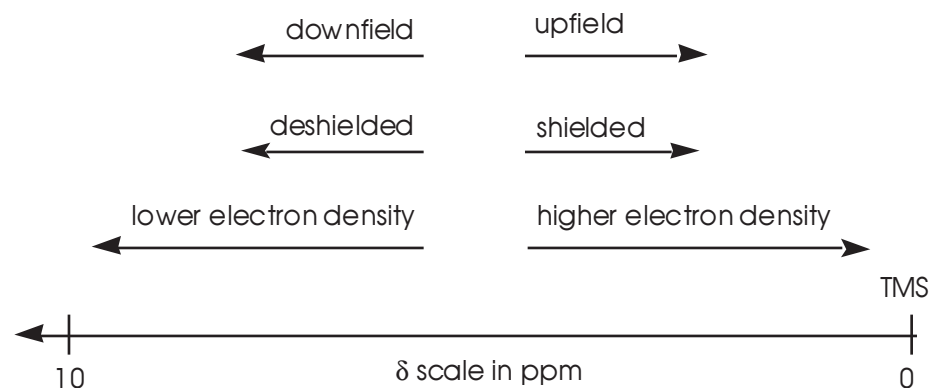
Surrounding electrons "shield" the proton under observation from the applied, or external field.

3. **Hydrogen, or proton**, is the most extensively studied nucleus due to its high natural abundance (100%) and widespread presence in organic molecules. In a given molecule different types of protons are surrounded by different degrees of electron density, and therefore experience different degrees of electron “shielding” in an NMR experiment.

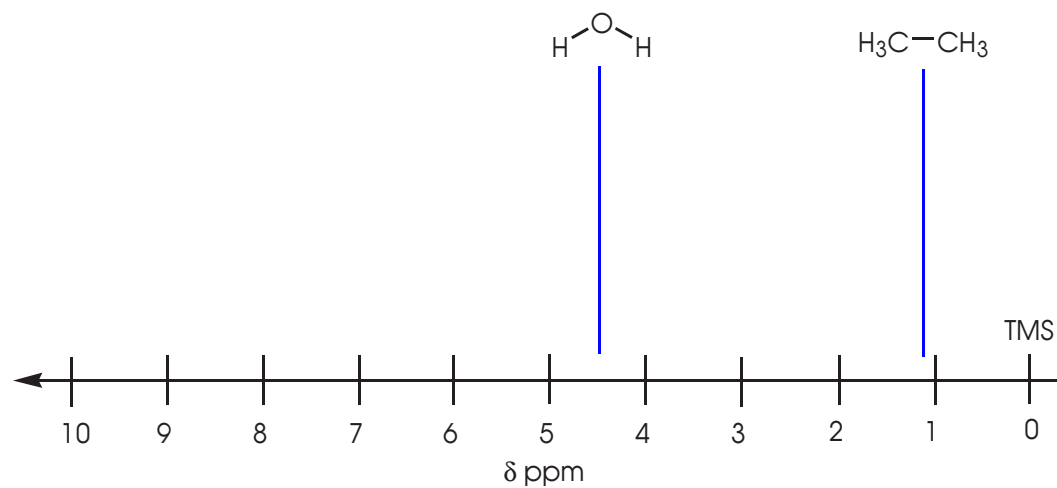
4. Protons which are in areas of high electron density, such as the hydrogen atom in NaH, are more highly shielded. They will experience a weakened external magnetic field relative to protons which are in areas of low electron density (and therefore less shielded) such as the hydrogen atom in HCl. As a result, the proton in NaH will require energy of lower frequency to achieve resonance than the proton in HCl, which is exposed to the full strength of the external magnetic field.

5. The difference in resonance frequency between chemically different types of protons forms the basis for their differentiation and is called the **chemical shift**. The chemical shift scale has experienced several changes over the years. Most changes are designed to standardize the results of NMR experiments performed with different magnets under different conditions. In this way, a given molecule will turn the same chemical shift values regardless of whether the experiment was performed on different instruments or under different conditions.

6. The currently used chemical shift scale is called the δ **scale**. In this scale the x-axis represents the chemical shift of the proton under observation relative to a standard called tetramethylsilane, or **TMS**. The chemical shift value is reported in parts per million (**ppm**). The proton absorption for TMS is always assigned an arbitrary value of zero ppm. All other protons in the spectrum are then referenced to the TMS peak. The δ -scale increases from right to left and has a typical range of about 10-12 ppm for most common organic compounds. The y-axis in the δ -scale represents the intensity of the absorption.



7. In the δ -scale more highly **shielded protons appear at lower δ values**, whereas relatively **deshielded protons appear at higher δ values**. Therefore protons attached to carbon, which is less electronegative than oxygen, will be more shielded and will typically appear around 1 ppm. Protons attached to oxygen, or those which are relatively close to more electronegative atoms, will be deshielded and will appear at higher δ values, as shown below for the . Refer to your textbook for more examples.



8. The NMR spectrum of methanol exemplifies this effect in a single molecule. The protons attached to carbon produce a signal located higher upfield (lower δ value) than the proton attached to oxygen.

