3. Protons attached to heteroatoms are highly variable and sometimes absent.

\[
\text{RO} - \text{H} \\
\text{PhO} - \text{H} \\
\text{RCO}_2 - \text{H}
\]
4. The chemical shifts of protons attached to sp²-hybridized carbons are affected by substituents bonded to the π-system.

** The protons ortho and para to electron donating and electron-withdrawing groups on a benzene ring show distinct upfield and downfield shifts:

![Chemical Structures](image)

** Electron donating and electron withdrawing groups also affect peak position of protons bonded to alkenes:

![Chemical Structures](image)
Q. **Why are peaks in HNMR split?**
A. This is due to **spin-spin coupling**. We must consider the small local magnetic field caused by hydrogen nuclei on adjacent carbons.

**Example 1:**

Looking at $H_a$:
- $H_a$ is affected by $H_b$ because it is on an adjacent carbon. But $H_b$ exists in two spin states:
  - $H_a$ sees:
The magnitude of the nuclei splitting is called the **coupling constant J** and is usually reported in Hz.

**Example 2:**

\[ \text{H}_3\text{C} - \text{CH}_2 - \text{Br} \]

Consider \( H_b \) in detail:
If a hydrogen is adjacent to two different hydrogens, you can get complex splitting patterns:

**Example 3:**
Special features of spin-spin coupling:

a) Chemical shift equivalent protons don't couple to each other.

b) **N+1 Rule:** Protons with N equivalent H’s on adjacent carbons are split into N+1 peaks, with the area ratios given by the appropriate line of Pascal's Triangle.

<table>
<thead>
<tr>
<th># EQUIVALENT adjacent protons (N)</th>
<th># of peaks (multiplicity) (N+1)</th>
<th>Area ratios (Pascal’s Triangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 (singlet)</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2 (doublet)</td>
<td>1 1</td>
</tr>
<tr>
<td>2</td>
<td>3 (triplet)</td>
<td>1 2 1</td>
</tr>
<tr>
<td>3</td>
<td>4 (quartet)</td>
<td>1 3 3 3 1</td>
</tr>
<tr>
<td>4</td>
<td>5 (quintet)</td>
<td>1 4 6 4 1</td>
</tr>
<tr>
<td>5</td>
<td>6 (sextet)</td>
<td>1 5 10 10 5 1</td>
</tr>
<tr>
<td>6</td>
<td>7 (septet)</td>
<td>1 6 15 20 15 6 1</td>
</tr>
</tbody>
</table>

• Splitting can be difficult to resolve if greater than 3 adjacent protons are present.

c) Two groups of protons coupled to each other must have the same J value (coupling constant).

Br₂CH–CH₂Br
• Unlike chemical shifts, which are measured in ppm (parts per million), coupling constants (J values) are measured in Hz. To get J values in Hz, take the chemical shift difference and multiply it by the operating frequency of the spectrometer.

• The signals for each are often point towards each other, distorting the idealized relative peak intensities.

d) When hydrogen atoms of similar chemical shift interact, complex patterns arise, and the signal appears as a multiplet.

e) The magnitude of the coupling constant is somewhat diagnostic of the relative spatial orientation of the coupling nuclei.
f) Under usual conditions, an OH proton does **not** split the NMR signal of adjacent protons, and the signal due to an OH proton is **not** split by adjacent protons:

\[
\text{CH}_3\text{CH}_2—\text{OH}
\]

**Why?** Protons on electronegative elements rapidly exchange between molecules in the presence of trace amounts of acid or base. It is as if the CH\(_2\) group in ethanol never “feels” the presence of the OH proton because the OH proton is moving so rapidly from one molecule to the other.  

**How?**

(If care is taken to remove all traces of acid and base, splitting will occur)
g) **Resolution:** Many compounds give spectra whose protons absorb so close to each other that their multiplets overlap. In addition, when two or more protons split each other by a coupling constant that is nearly as large as their chemical shift separation, *second-order effects* can alter the shapes of the multiplets, making them difficult to interpret. Some of these issues can be resolved by going to higher spectrometer frequencies and magnetic fields.

**Q.** Both spectra are plotted on a δ 0 – 10 scale, so the peaks come at the same positions, but the splitting appears to be smaller in the 300MHz instrument. But chemical shift and coupling constants are constant! How can this be?