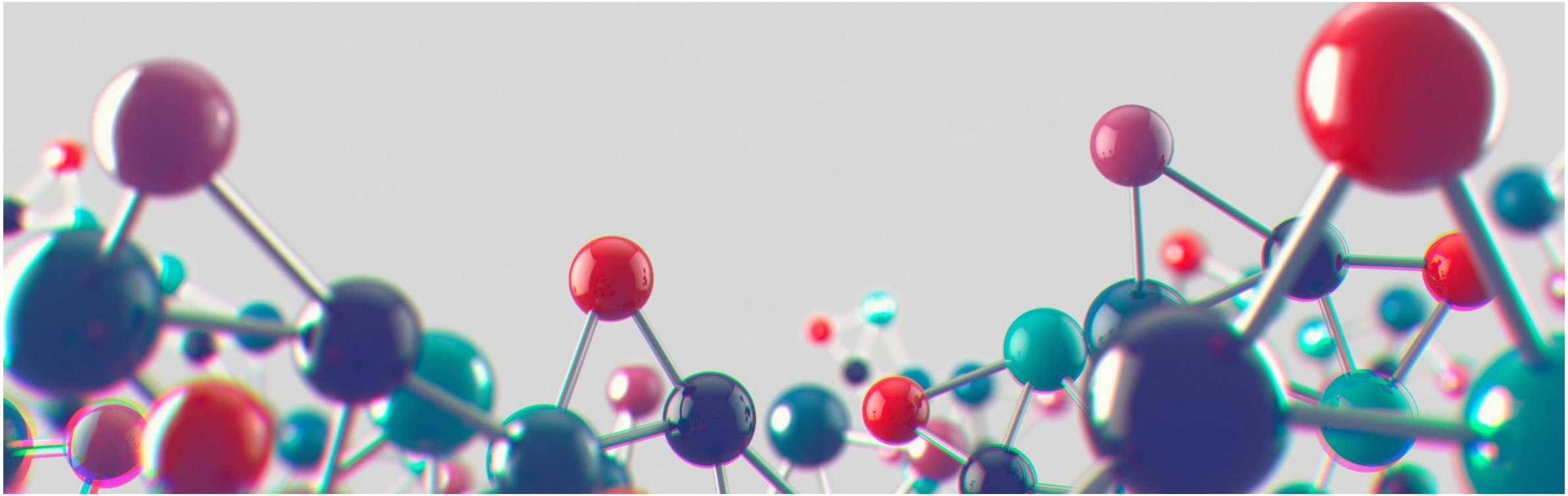


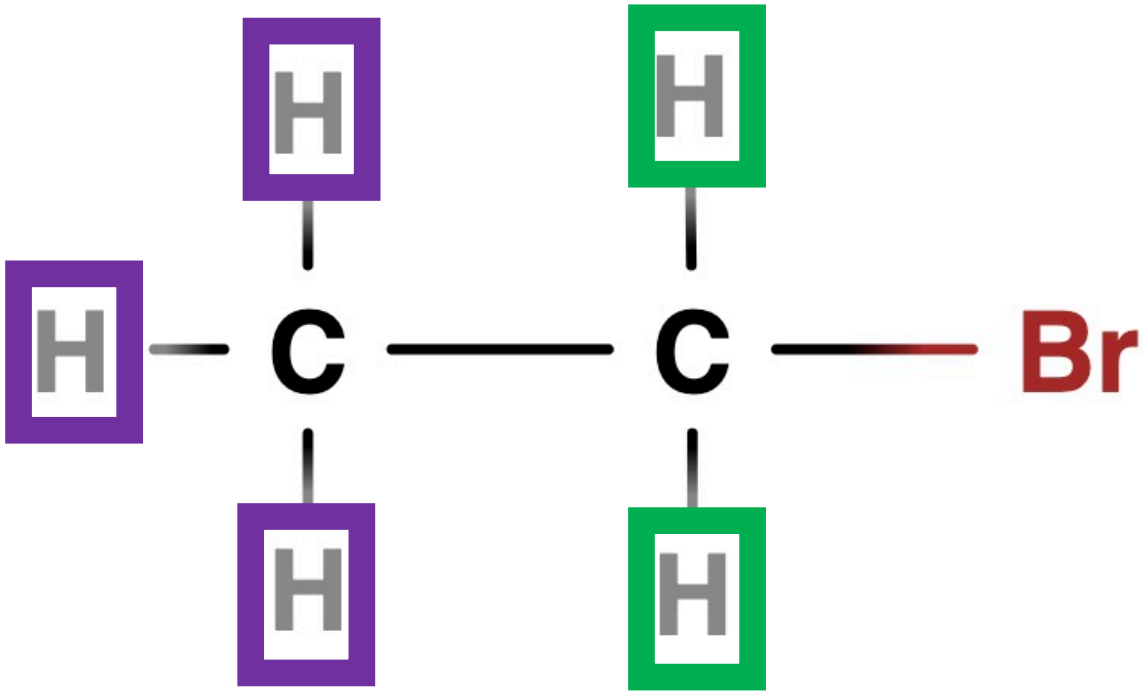
NMR THEORY – CHEMICAL SHIFT

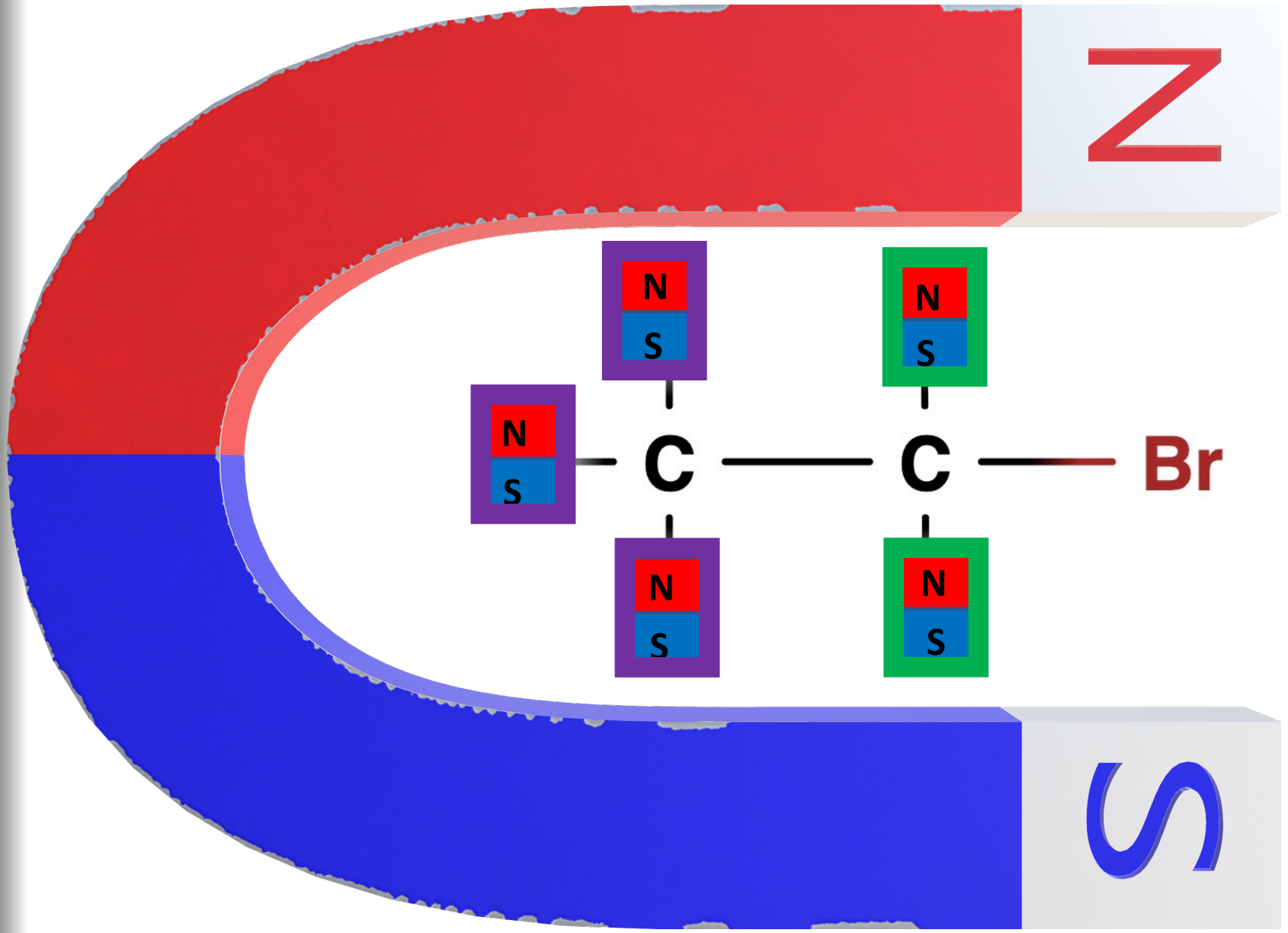
ChemistryTuition.Net

How does NMR work?

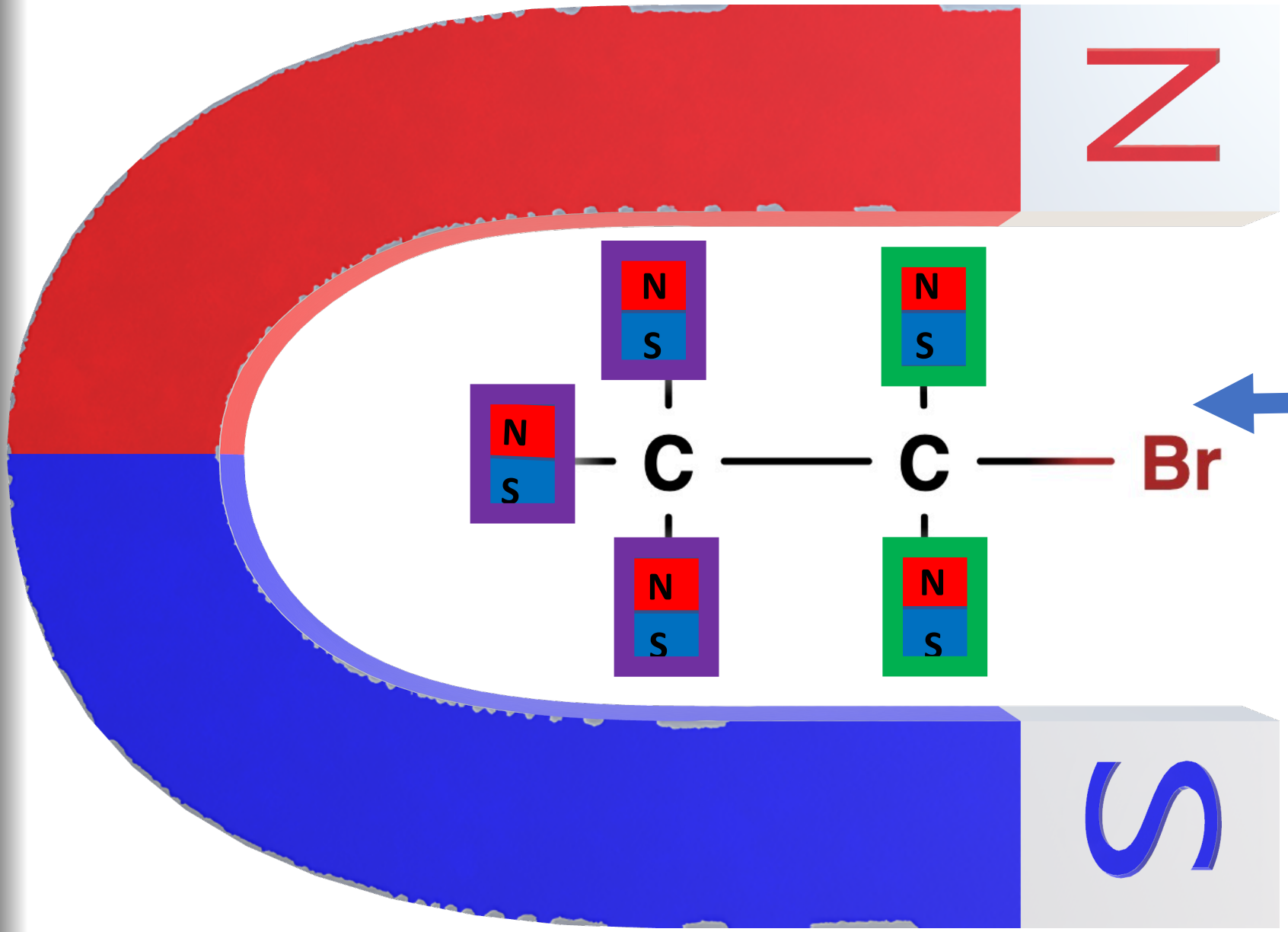
- The protons and neutrons that make up the nucleus are arranged in energy levels, just like the electrons that orbit around it. Like electrons, protons and neutrons possess spin.
- The spins of the protons and neutrons can be paired or unpaired. If all are paired, the spins cancel and the nucleus does not have an overall spin.
- In a nucleus with an odd number of protons and neutrons, such as ^{1}H (1 proton and 0 neutrons) or ^{13}C (6 protons and 7 neutrons), the nucleus is left with unpaired spins and has an overall spin of ½ and behave like bar magnets with a north and south pole.

Consider the hydrogen atoms in bromoethane – you will recognize from your A level studies that there are two environments for the H nuclei.

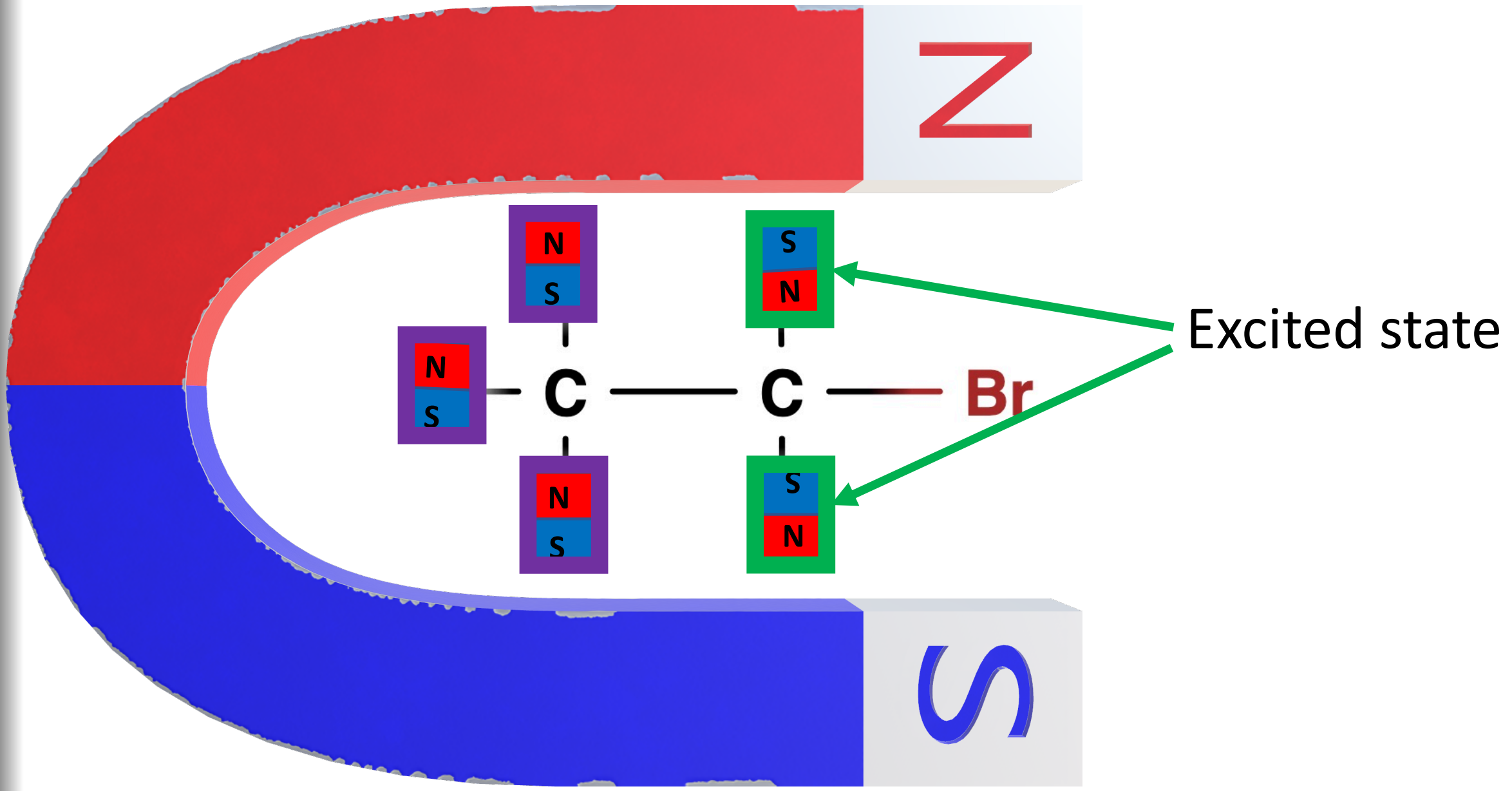


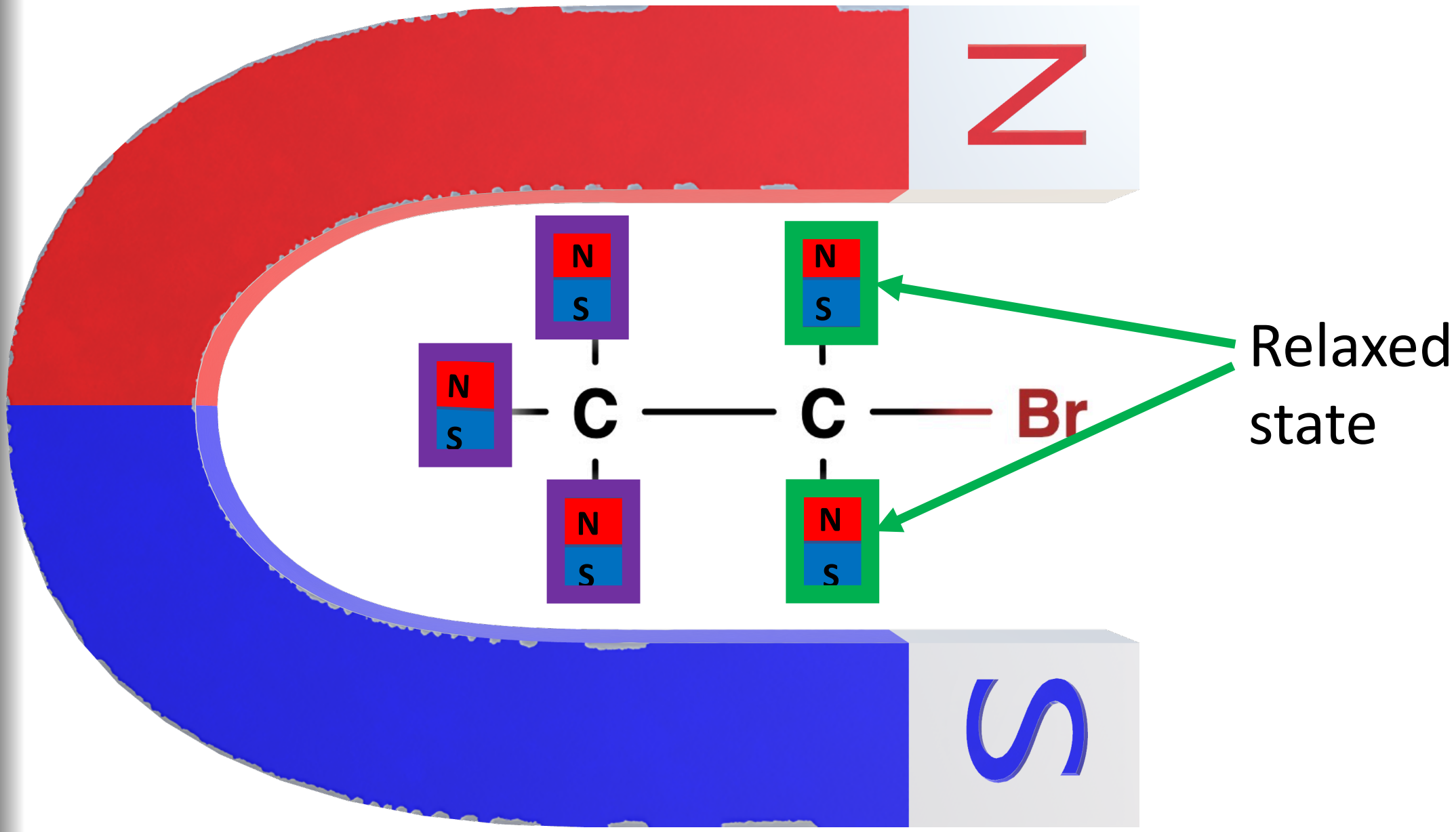


If an external magnetic field is applied, then the magnetic fields of the nuclei will align with the external field to give the lowest energy orientation.



If the correct frequency of electromagnetic radiation is now applied, the nuclei will absorb it and flip to the higher energy state.


N
S
N
S
C
C
Br
S
N
S
N
S
N
N
S
Excited state


N
S
N
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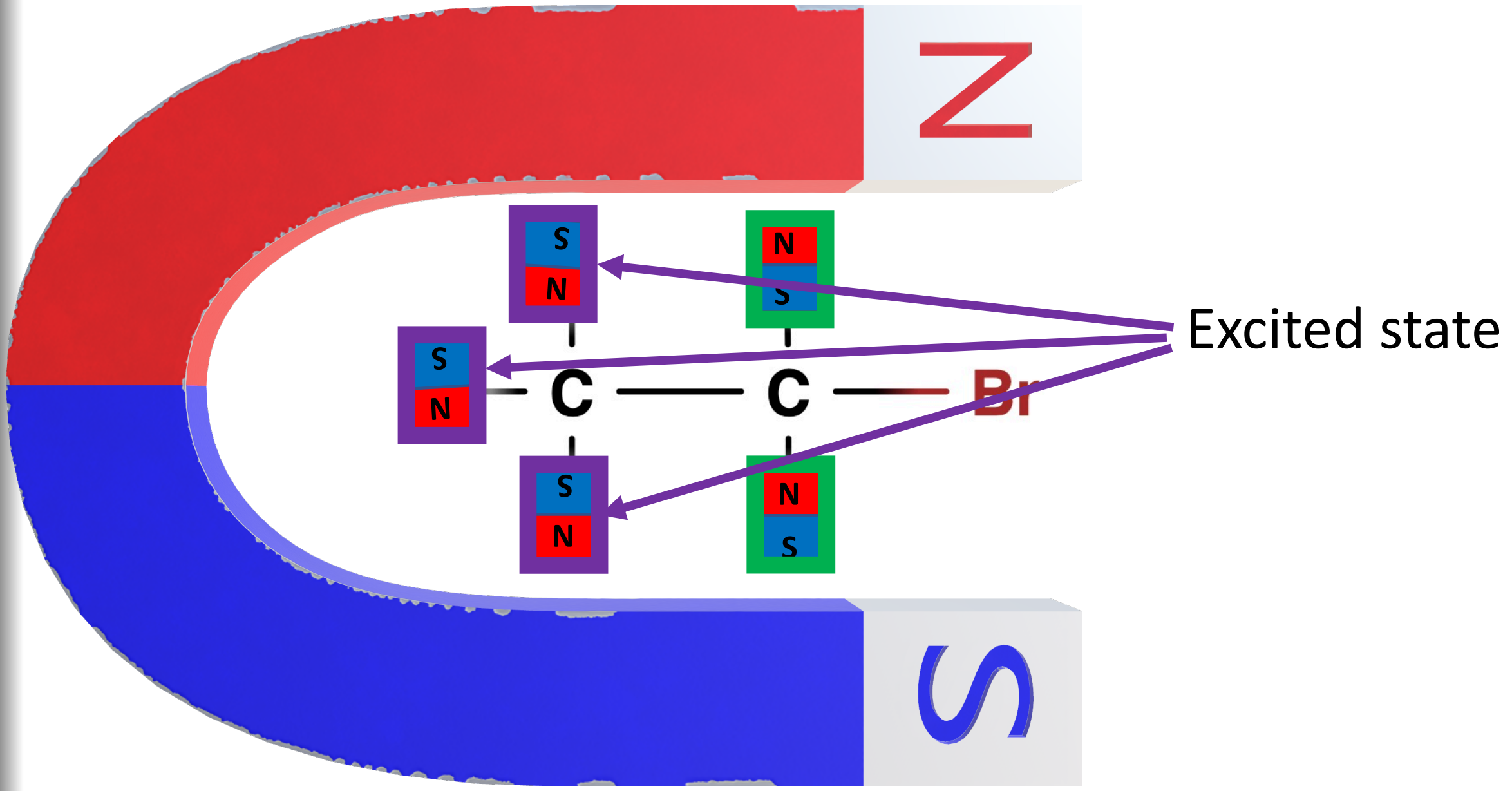
N
S
N
S
C
C
Br
N
S
N
S
Relaxed
state


N
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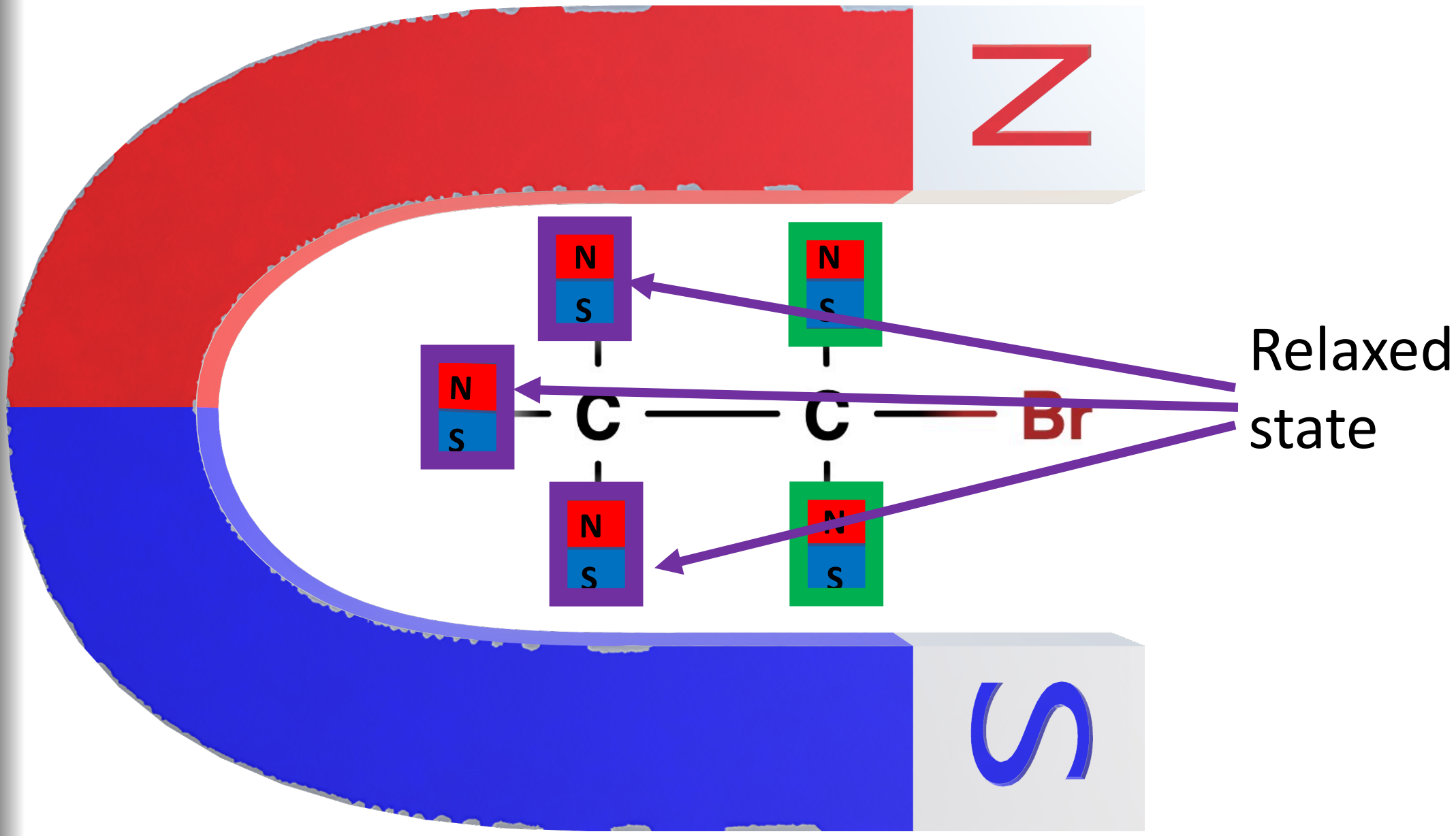
S
N
C
C
Br
S
N
N
S
Excited state


N
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N
S
C
C
Br
N
S
N
S
Relaxed
state

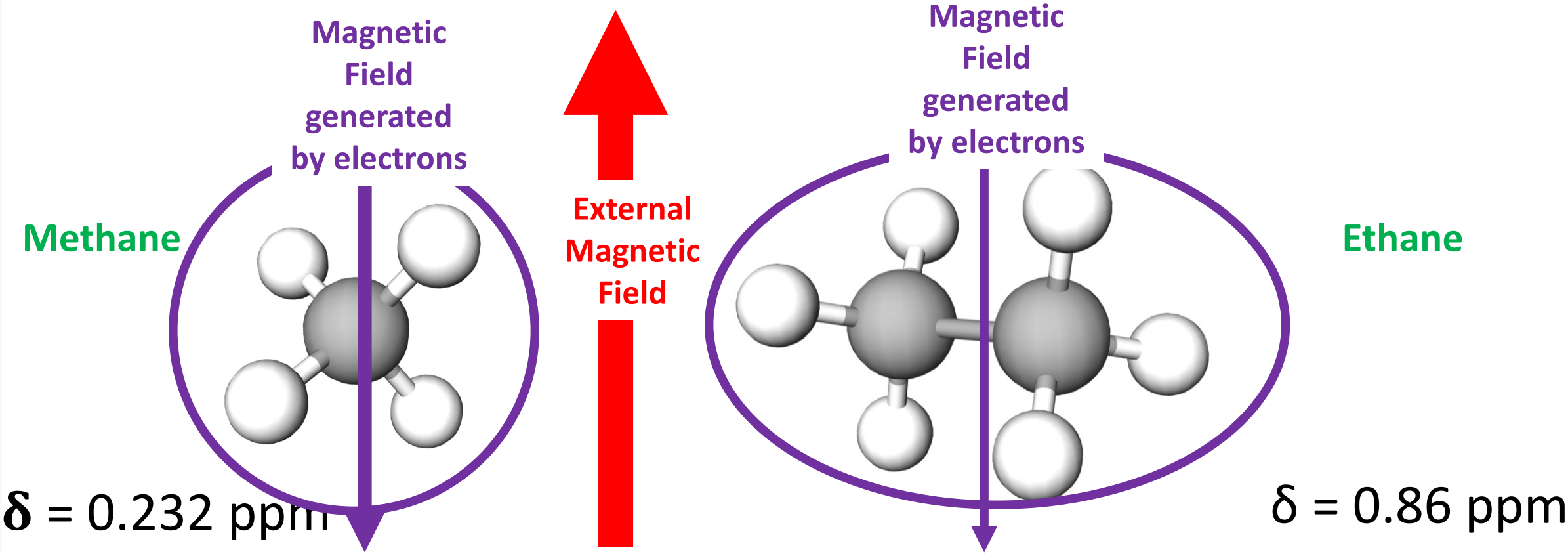
Chemical Shift

The two frequencies are quoted as chemical shift values ($\boldsymbol{\delta}$) measured in ppm on a scale of 0 to 12.
This compares Frequency 1 and 2 against the frequency required to excite ^{1}H nuclei in $Si(CH_4)_4$ (Tetramethylsilane or TMS).
When running an NMR, TMS is added to the sample. The NMR machine will then record the absorption frequency for the ^{1}H nuclei in TMS as 0 ppm.

$$\boldsymbol{\delta} \text{ in ppm} = \frac{\text{Frequency of signal} - \text{Frequency of TMS}}{\text{Frequency of spectrometer}} \times 10^6$$

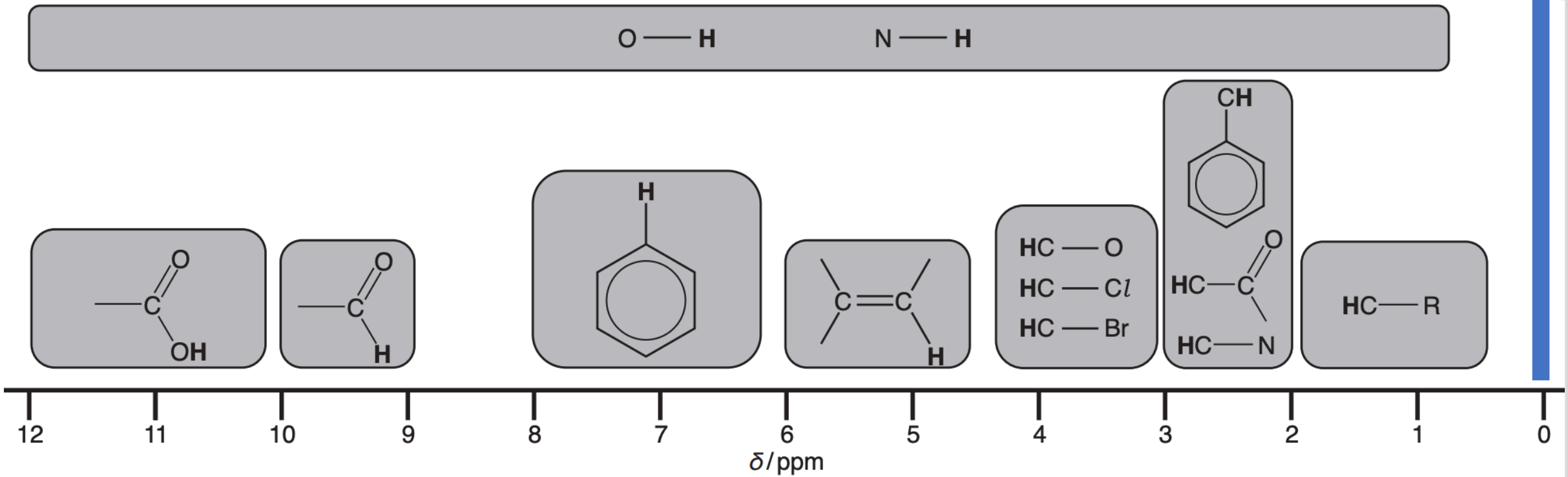
What causes the different frequencies?

Electrons in the molecule generate their own magnetic field.
This field opposes the the applied magnetic field and so reduces the strength of the magnetic field experienced by the nucleus.



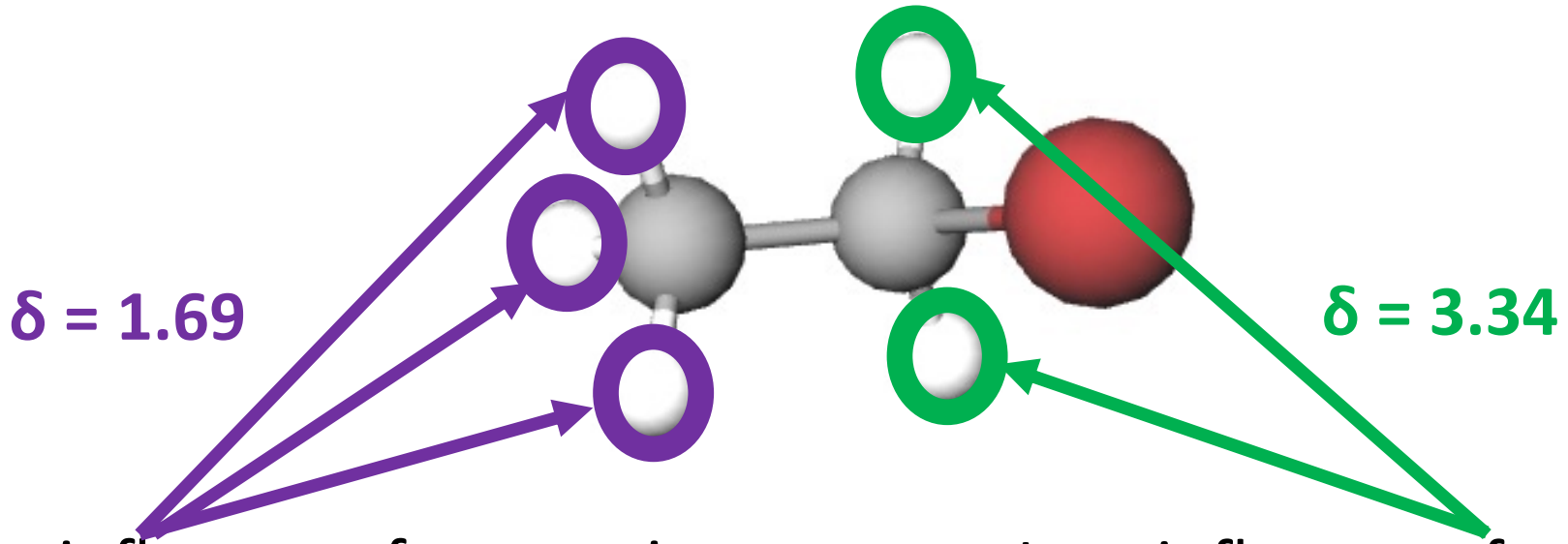
Shielding of the external magnetic field by the molecule's electrons **decreases**. The net magnetic field strength experienced by ^{1}H nuclei increases. Hence the value of the δ value increases.

TMS



Electron withdrawing groups **decrease** the electron density at the nucleus, **deshielding** the nucleus and result in a larger chemical shift.

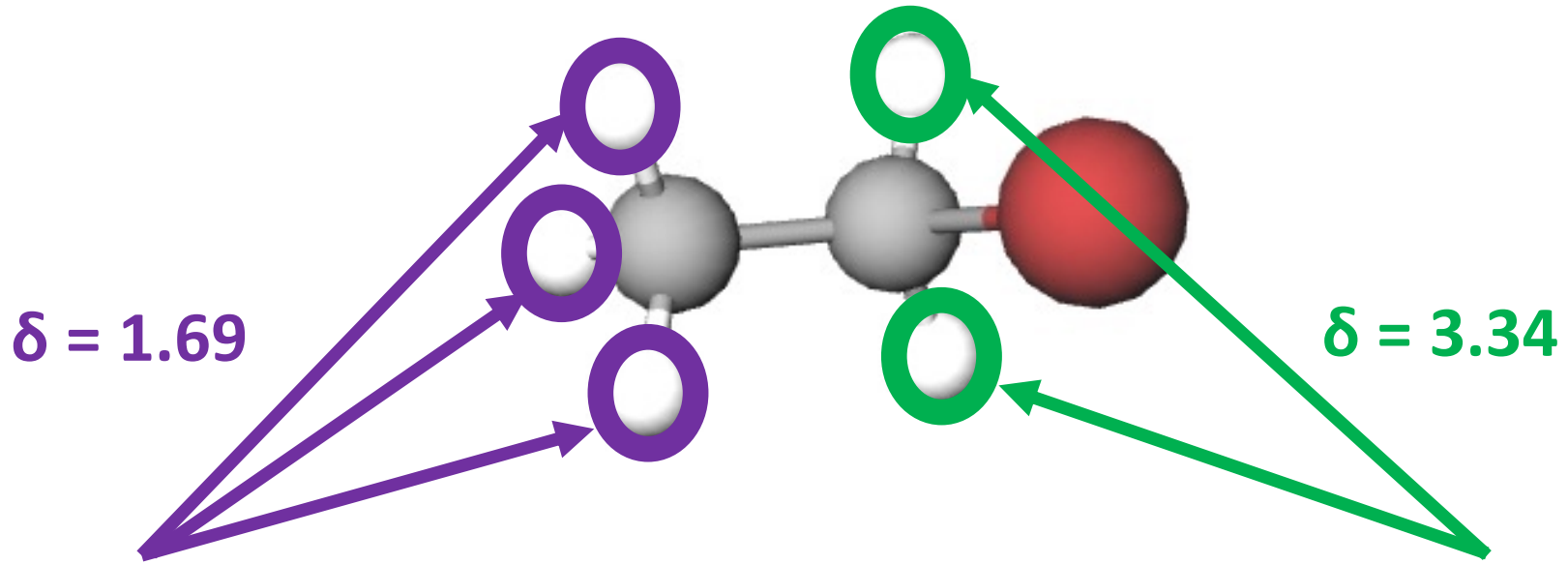
Bromoethane has two peaks in the ^{1}H nmr due to the two different magnetic fields experienced by the ^{1}H nuclei.



Greater influence of magnetic field generated by the molecule's electrons

Less influence of magnetic field generated by the molecule's electrons

Returning to bromoethane, we now know:



These nuclei are **more shielded** by the molecule's magnetic field.

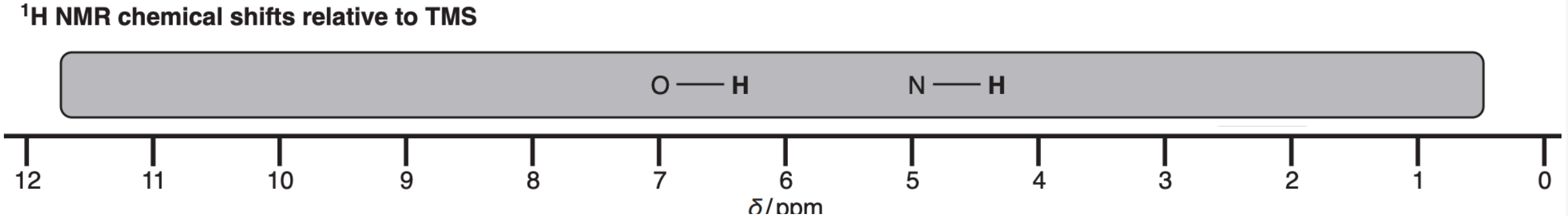
These nuclei are **more deshielded** due to Br's electron withdrawing effect

Comparison of different compounds:

CH_3X	Chemical Shift (ppm)	Electronegativity of X
CH_3F	4.26	4.0 (F)
CH_3OH	3.4	3.5 (O)
CH_3Cl	3.05	3.1 (Cl)
CH_3Br	2.68	2.8 (Br)
CH_3I	2.16	2.5 (I)
CH_4	0.23	2.1 (H)
$(CH_3)_4Si$	0	1.8 (Si)

Hydrogen Bonding

Hydrogen nuclei that are involved in hydrogen bonding (-OH or -NH) are usually observed over a wide range of chemical shifts.



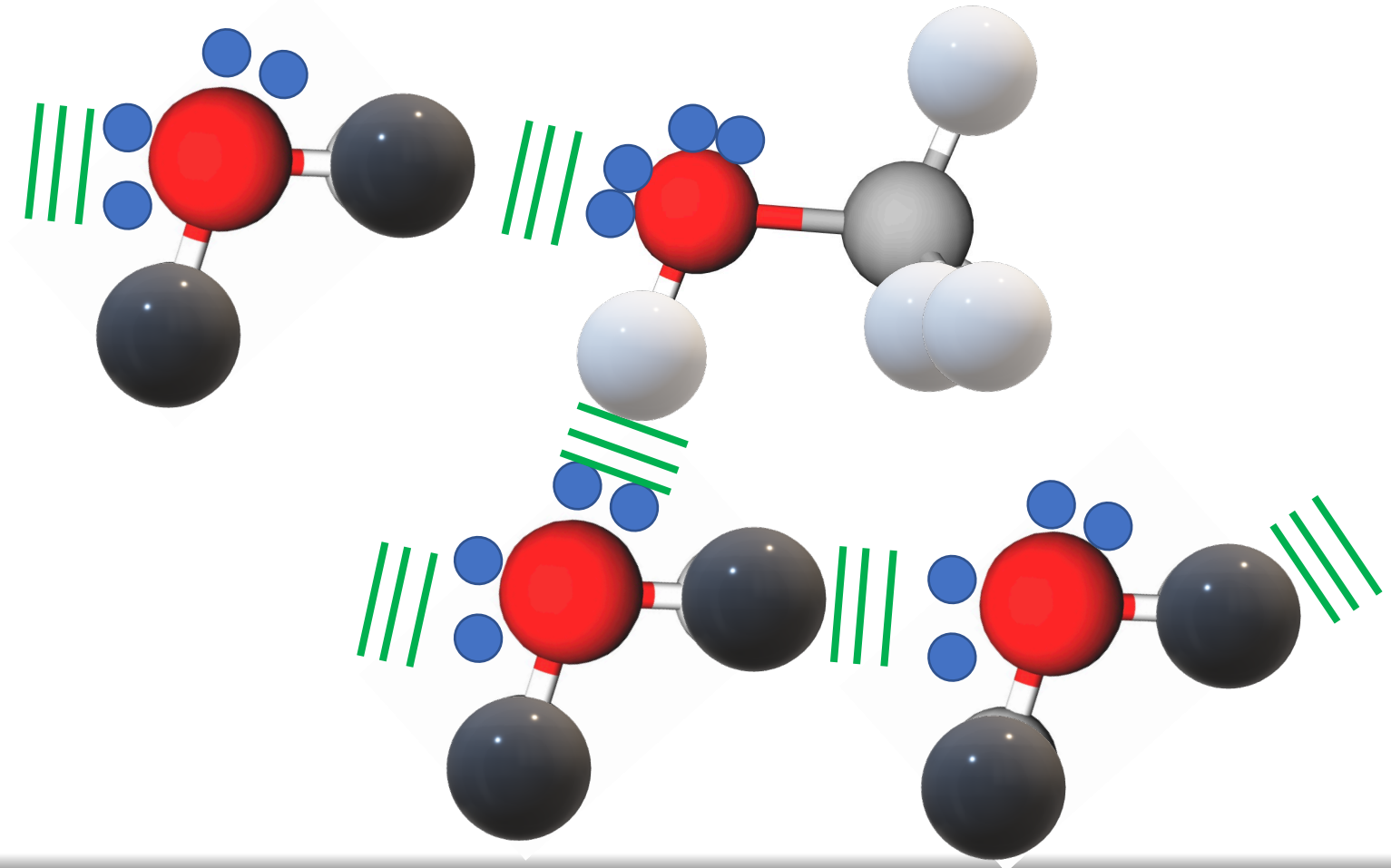
This is due to the deshielding that occurs in the hydrogen bond.

Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding.

Together with solvent effects, acidity, concentration and temperature this makes it very difficult to predict the chemical shifts for these atoms.

Using D_2O

If the nmr is run in D_2O, peaks due to NH and OH will disappear since ^2H does not have a spin and so no signal is observed in the nmr as ^1H are replaced by ^2H nuclei.



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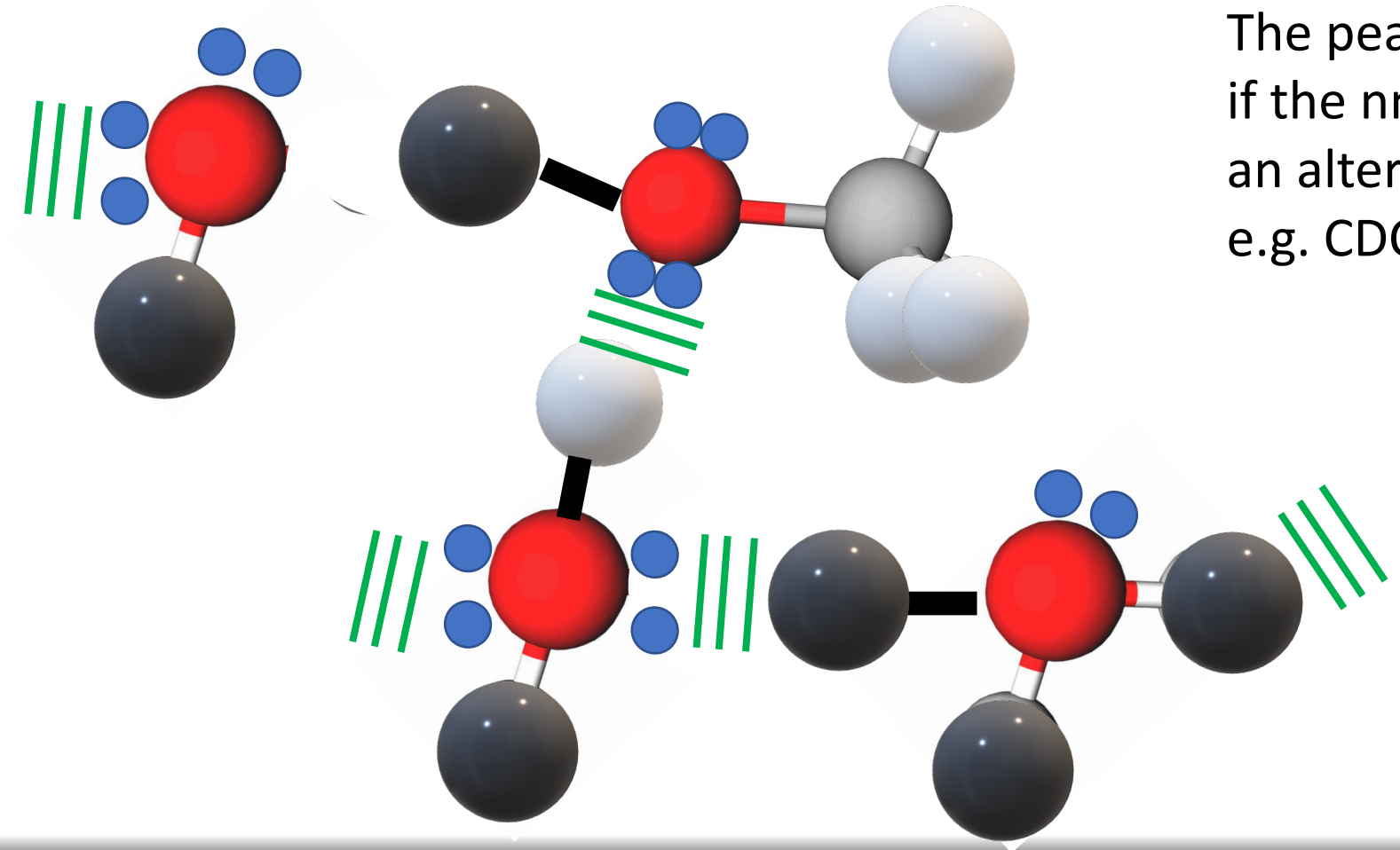

The peaks will reappear if the nmr is run using an alternative solvent e.g. $CDCl_3$