Nuclear Spin & Magnetic Moment

For NMR experiments, the Magnetic property of the nucleus is the basis for measurement.

- In protons, electrons, and neutrons, there is a spin, and therefore, a magnetic moment.

$$\vec{\mu} = \gamma \vec{I}$$, where $\vec{\mu}$ = magnetic moment
$\vec{I}$ = spin angular momentum
γ = gyromagnetic ratio

- NMR concerns the net spin of the nucleus, and requires that the net spin of the nucleus $\neq 0$. In this case, the nucleus can act as a magnet.

→ Atoms with net spin = $\frac{1}{2}$ have odd atomic mass numbers:
- ^{1}H, ^{13}C, ^{15}N, ^{31}P

→ Atoms with net spin = 1
- ^{2}H, ^{14}N

→ NMR inactive nuclei:
- ^{12}C, ^{16}O, (major species)
- Even protons + neutrons

$\vec{B_0}$

$$U = -\vec{B} \cdot \vec{\mu} = -\gamma \vec{B} \vec{I} = \gamma B_0 I_z$$

Nuclear spin denoted as I:

$I_z = m_I \hbar$

$I = \frac{1}{2}$, $m_I = -\frac{1}{2}, +\frac{1}{2}$

Operator rules are the same as for spin.

$\hat{I}_z \alpha = \frac{\hbar}{2}\alpha$

$\hat{I}_z \beta = -\frac{\hbar}{2}\beta$

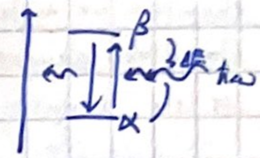
$\hat{I}_y \alpha = \frac{i\hbar}{2}\beta$ $\quad$ $\hat{I}_x \alpha = \frac{\hbar}{2}\beta$

$\hat{I}_y \beta = -i\frac{\hbar}{2}\beta$ $\quad$ $\hat{I}_x \beta = \frac{\hbar}{2}\alpha$

$$U = -\gamma B_0 \hbar \begin{Bmatrix} \frac{1}{2} \\ -\frac{1}{2} \end{Bmatrix}$$

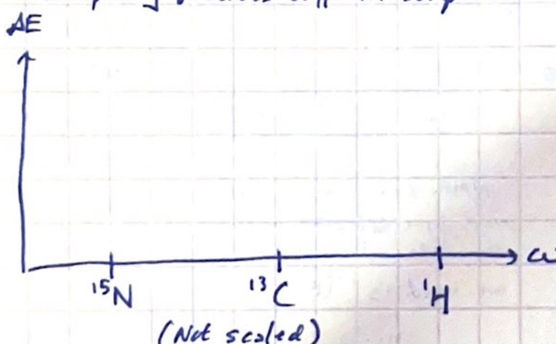
$\alpha = -\gamma B_0 \hbar \frac{1}{2}$ (corresponds to lower energy)

$\beta = \gamma B_0 \hbar \frac{1}{2}$ (corresponds to higher energy)



$\Delta E = \hbar \gamma B_0$ → ΔE is dependent, therefore on γ and the magnetic field, B_0. The frequency associated with this transition ΔE is $\omega = \gamma_0 B_0$

Comparing γ across different compounds:



(Not scaled)

$\gamma_H > \gamma_{^{13}C} > \gamma_{^{15}N}$ → More specifically, $\gamma_{^{13}C} \sim \frac{1}{4}\gamma_{^1H}$ and $\gamma_{^{15}N} \sim -\frac{1}{18}\gamma_{^1H}$

Recall that for a transition from $1 \to 2$,

$$W = \frac{2\pi}{\hbar}\rho(\Delta E) B_0 \left| \int \psi_2^* \mu \psi_1 \, dx \right|^2$$ When the spin or magnetic moment is 0, the term $\left| \int \psi_2^* \mu \psi_1 \, dx \right|^2 = 0$.

Therefore, in order for $W \neq 0$,

1) The spin quantum number of the nucleus, $I \neq 0$.
2) $B_0 \neq 0$
3) The unperturbed hamiltonian, $\hat{H} = \hat{H}_0$ must turn into $\hat{H} = \hat{H}_0 + \hat{H}_{int}(t) = \mu$

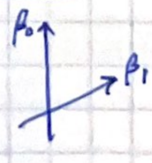
$\left| \int \psi_2^* \mu \psi_1 \, dx \right|^2$ where $\psi_2^* = \beta$ and $\psi_1 = \alpha$

↳ $\hat{H}_0 + \hat{H}_{int}(t)$

$-\vec{B}_1 \vec{\mu} = \gamma \vec{B}_1 \vec{I}$ → $(-\vec{B}_1 \vec{\mu}) \cos \omega t$ ← Oscillation effects

Magnetic field

4) $\Delta m_I = \pm 1$



$$\gamma \vec{B}_1 \vec{I} = \gamma (B_{1x} I_x + B_{1y} I_y + B_{1z} I_z)$$

$$\int \beta^* \hat{I} \alpha \, d\sigma$$

$\int \beta^* \hat{I}_x \alpha \, d\sigma$ $\quad$ $\int \beta^* \hat{I}_y \alpha \, d\sigma$ $\quad$ $\int \beta^* \hat{I}_z \alpha \, d\sigma$

$\frac{\hbar}{2}\int \beta^* \beta \, d\sigma = 1$ $\quad$ $\frac{\hbar}{2}\int \beta^* \beta \, d\sigma = 1$ $\quad$ $\frac{\hbar}{2}\int \beta^* \alpha \, d\sigma = 0$

Nonzero terms - can cause a transition dipole

As long as B_1 has an x-component, a transition will occur: $B_1 \perp B_0$

Is NMR dangerous? How much energy is generated from its magnetic field?

$B_{earth} \sim 5\times10^{-5}\,T$, where $1\,T = 1\frac{kg}{As^2}$

$MRI \sim 1-5\,T$

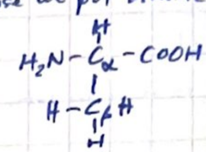
$NMR \sim 19\,T,\ 800\,\mu Hz$ (400,000 times stronger than B_{earth}!)

$$\Delta E = h\nu = \gamma\hbar B_0 = (6.626\times10^{-34}\,J\cdot s)(800\cdot10^{6}\,\tfrac{1}{s}) = \underline{5.3\times10^{-25}\,J} = \Delta E_{NMR}$$

Compare to $k_B T$ at 300K: $(1.4\times10^{-23}\,J/K)(300\,K) = 4.2\times10^{-21}\,J$: $\frac{\Delta E_{NMR}}{k_B T} \approx 1.3\times10^{-4}$

This value is 4 orders of magnitude smaller than thermal motion - no, this should not be harmful.

Suppose we put alanine in the NMR:



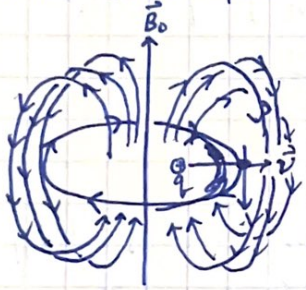
7 H, 1 N → NMR active

3 C, 2 O → Not NMR active.

We would expect to see:

But this is not the actual result obtained. Why is this the case?

The nucleus is surrounded by an e^- ~~field~~ cloud, therefore we neglect to consider that the e^- charges also generate an electric field, known as the "Lorentz force"



$\vec{B}_{induced} = \vec{F} = q\vec{v}\times\vec{B}$

where

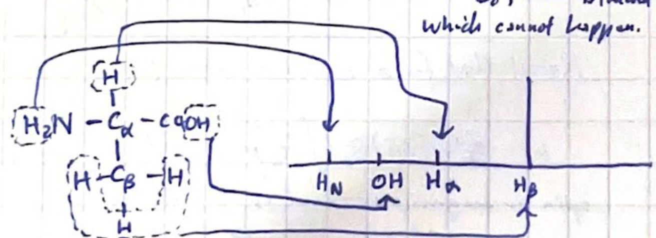
$\vec{B} = \vec{B}_0 + \underbrace{\vec{B}_{induced}}_{\sim\vec{B}_0}$ → Therefore, $-\vec{B}_0 \rightarrow -\vec{B}_0\sigma$

shielding factor

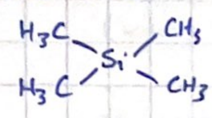
(Not spin)

if we remove $\vec{B}_0$, then $\vec{B}_{induced}=0$ which cannot happen.

$$\boxed{\omega = \gamma B_0(1-\sigma)}$$



NMR can come at different ω, so we must have ~~different~~ references to compare the data collected: the reference molecule we used is TMS:



, highly shielded

$\omega = \gamma B_0(1-\sigma)$

$\omega_{ref} = \gamma B_0(1-\sigma_{ref})$ (For TMS)

$\hookrightarrow \frac{\omega-\omega_{ref}}{\omega_{ref}}$ (Correction) $\rightarrow \frac{\cancel{\gamma B_0}(\sigma_{ref}-\sigma)}{\cancel{\gamma B_0}\underbrace{(1-\sigma_{ref})}_{\approx 10^{-6}}} \rightarrow \underline{(\sigma_{ref}-\sigma)\cdot10^{6}}$ → By definition, chemical shift of TMS = 0.

$\hookrightarrow$ Chemical shift (from reference) units of ppm.