Nuclear Spin

- Some nuclei have Zero spin
  - ^{12}C, ^{16}O: $I = 0$
- Many important nuclei have **$I = ½$**
  - **^{1}H**, **^{13}C**, **^{31}P**, ^{15}N etc.
- Some have larger spins
- $I = 1$: ^{14}N, ^{2}H; $I = 3/2$: ^{11}B, ^{7}Li, ^{23}Na; $I = 3$: ^{10}B
  - if no. of neutrons **and** no. of protons are both even, then the nucleus has **NO** spin; $I = 0$
  - If no. of neutrons + protons is odd, then I is half-integer (1/2, 3/2 etc.).
  - If no. of neutrons **and** no. of protons are both odd, then I is integer.

Spin States

- Value of I determines number of spin states: different ways of spinning, labelled m_I.

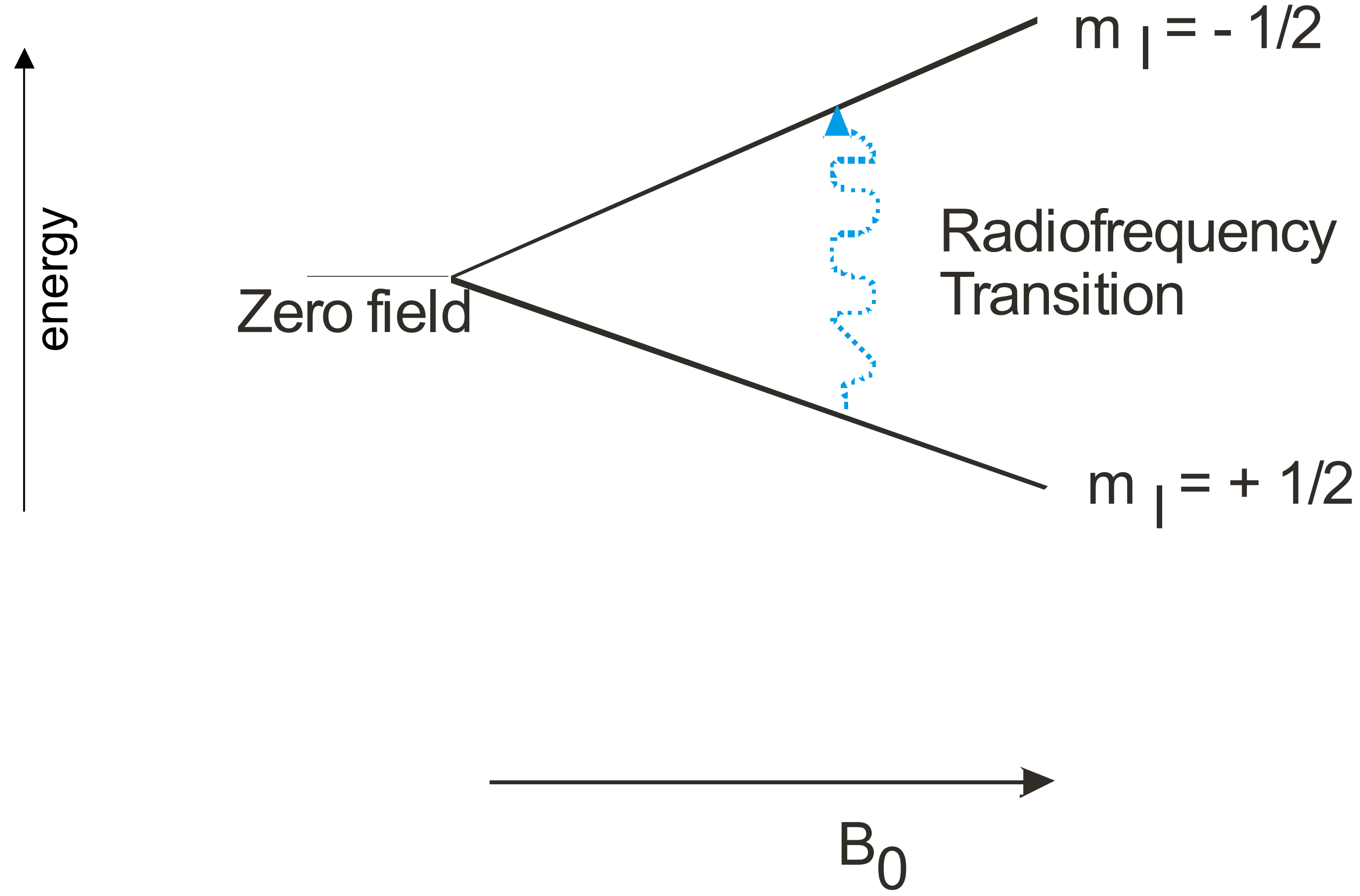
m_I can have values –I, -I + 1,……I

eg. $I = ½$, m_I = **- ½ , + ½**

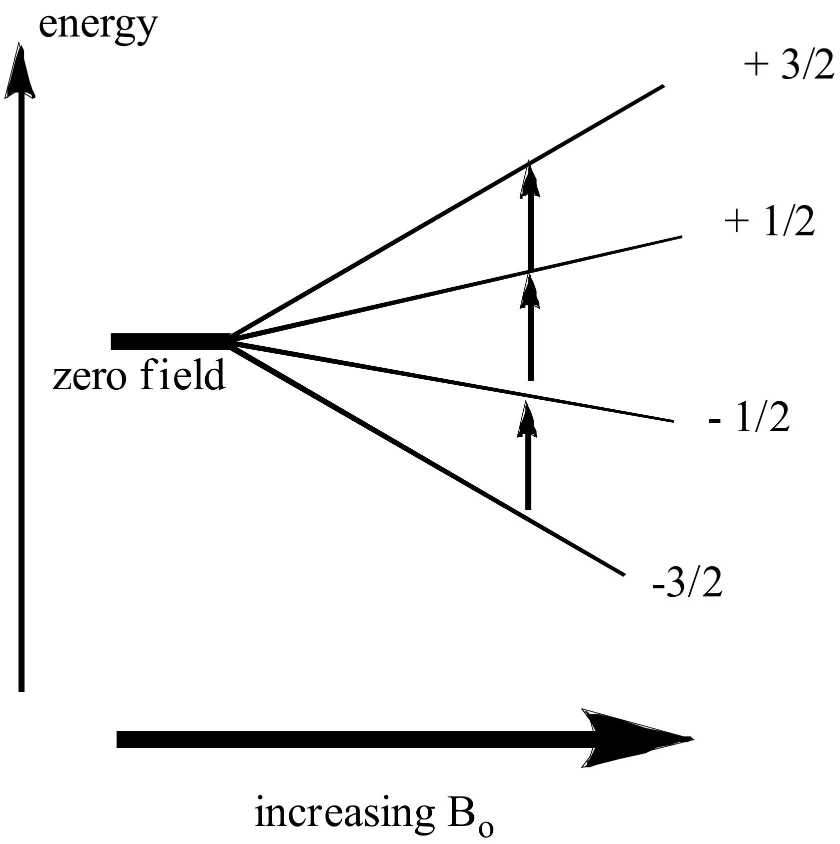
$I = 3/2$, $m_I = - 3/2 , - ½, + ½, + 3/2$

- All are usually of equal energy. Nuclear spin has no consequences UNLESS….
- Apply a ***Magnetic field***.
- A spinning charged particle (nucleus) generates its own magnetic field. If an external magnetic field is applied, then the nuclei can align their fields with the applied field, or they can oppose it: Now of DIFFERENT ENERGY.

Effect of Applying Magnetic Field B_0 on Energy of Spin states



I = 3/2 nucleus: observe



- Selection rule:

Δm_I = +/- 1.

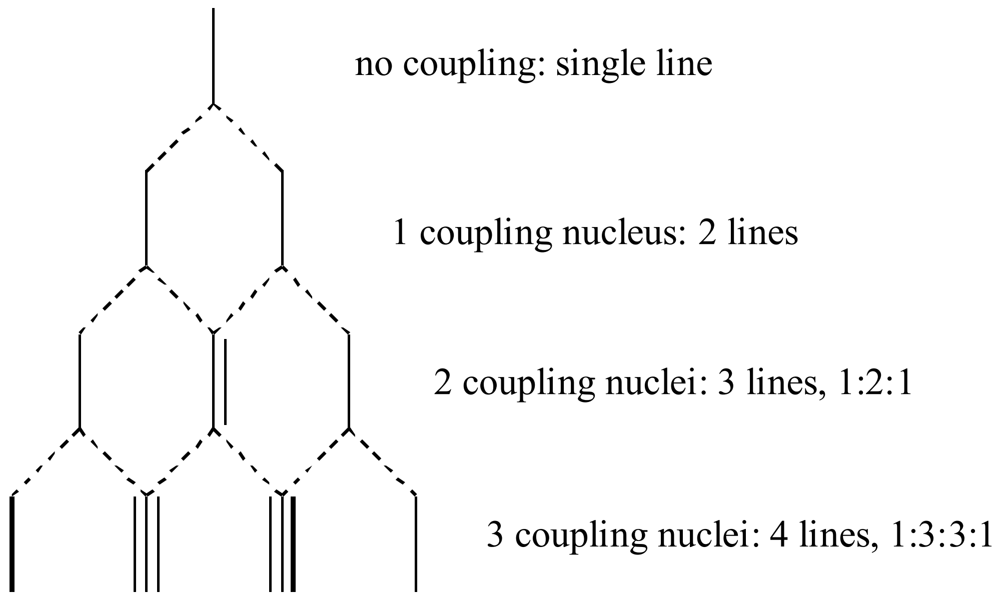
All transitions are of same energy: still **only 1 line** when OBSERVING I = 3/2 nucleus.

BUT causes more splitting when coupling to other nuclei….

Multiplet Patterns

- Multiplicity: Coupling of observed environment to ***n*** nuclei of spin I gives

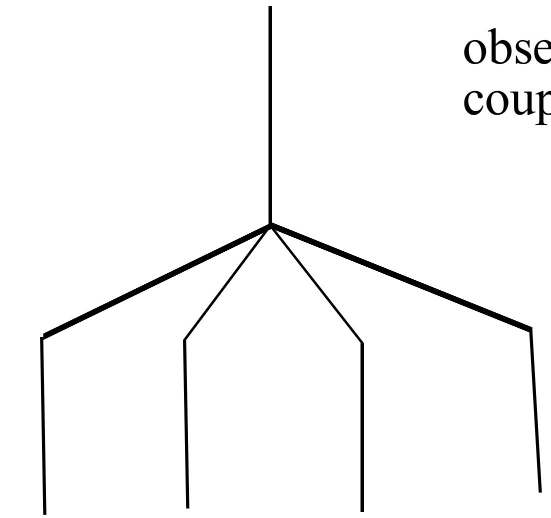
2*n*I + 1 lines. For I = ½, this simplifies to **n + 1** lines. Relative intensities follow Pascal's triangle:



Coupling patterns for I = ½ nuclei

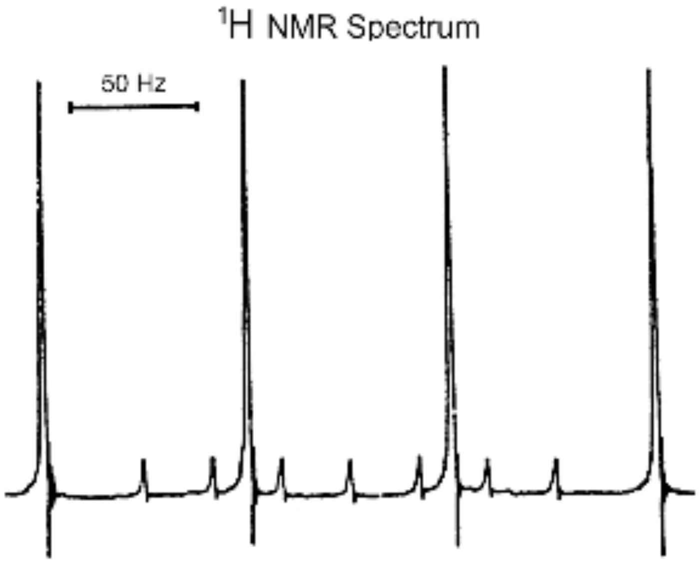
Coupling: I = 3/2

- Observe a nucleus of any spin, which is coupling to I= 3/2……



Coupling to 1 I = 3/2 nucleus:
4 lines

Example: BH_4^- ***free anion*** in solution



- Sharp 1:1:1:1 quartet
- 4 equivalent Hydrogens coupling to ^{11}B, $I = 3/2$
- Sharp, because of high symmetry of T_d BH_4 anion
- If symmetry is broken, e.g. by **co-ordination** of BH_4 to a metal, will generate an **electric field gradient** around the boron.
- I > ½ nuclei are quadrupolar.
- Nuclear quadrupole interacts with electric field gradient, gives faster relaxation
- Faster relaxation gives BROADER LINES.

NMR vs IR

- NMR relaxation time, even for quadrupolar nucleus, is a few hundred milliseconds.
- A long time in spectroscopic terms
- Sometimes see an **average over time** of the environment of the nucleus.
- Contrast IR: VERY short timescale. Always see a **snapshot** of the environment.

Avoiding confusion with multinuclear NMR

- Ask yourself 3 simple questions
  1. What nucleus am I look at?
  2. How many peaks?

     (answer gives number of different environments for that nucleus; may be smaller over time than at any instant, if different environments are chemically exchanging)
  3. What couplings do I see ($2nI + 1$). Apply this separately for each nucleus that is coupling to the one you are observing.

  (proton decoupling can simplify things)