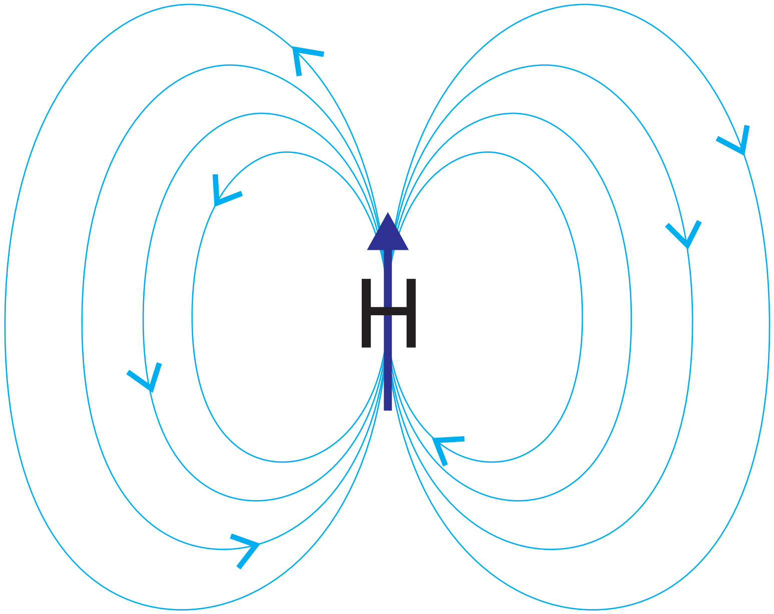
Nuclear Overhauser Enhancement (NOE)

NOEs arise from nuclear spin dipole-dipole interactions. All NMR-active nuclei (spin≠0) have a magnetic dipole, having a field similar to a bar magnet:

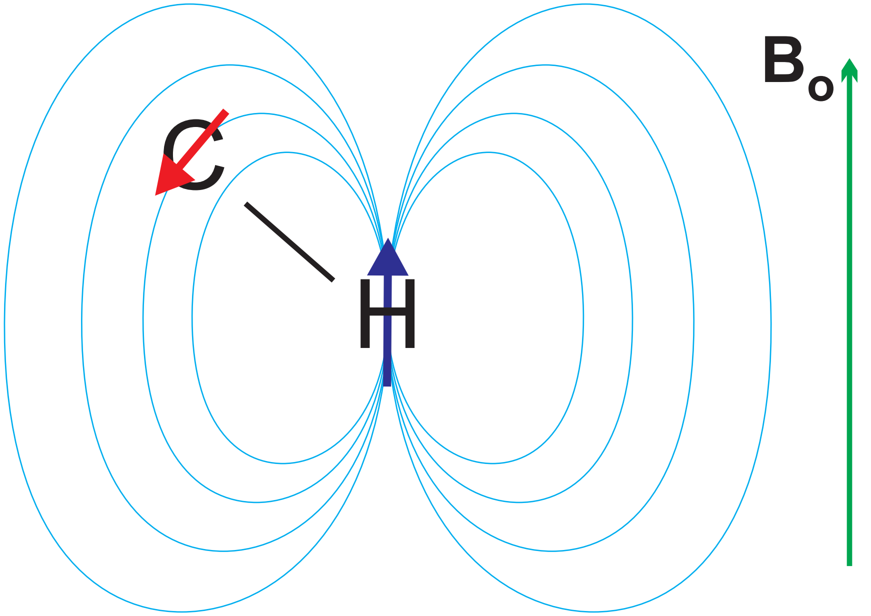


Nuclear Overhauser Enhancement (cont.)

A 13C nucleus will “feel” the presence of a 1H nucleus via the proton’s dipolar field.

In the case shown below, the dipolar field is ~30 degrees from being opposite of the applied static magnetic field.

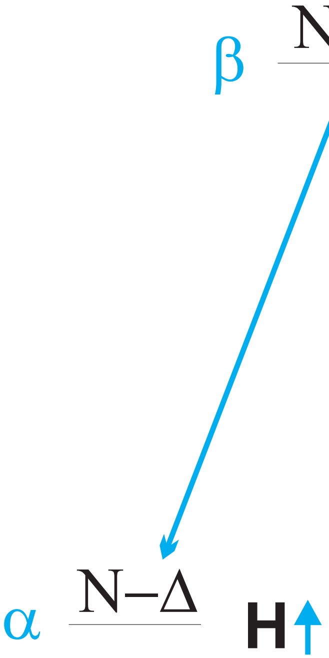
$$\Delta E_{dd} \propto \gamma_i^2 \gamma_j^2 \left\langle \sum_j \frac{\tau_c}{r_{ij}^6} \right\rangle_t$$



Population Description for Protons

$$\Delta E = \gamma_H B_o$$

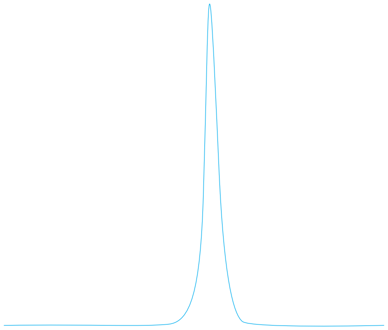
$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/RT} \sim 1 - \Delta E/RT$$



β $N+\Delta$ **H**↓

α $N-\Delta$ **H**↑

$\nu_o = 500\text{MHz}$



Population Description for Protons

Since $\Delta E/RT \ll 1$

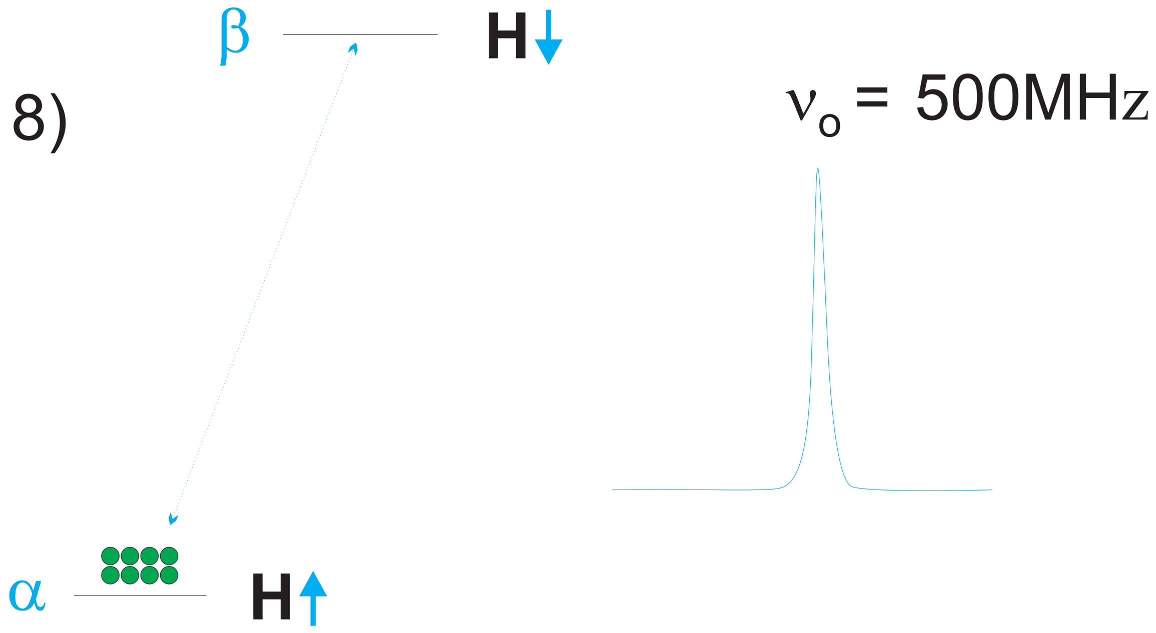
$N_\beta \sim N_\alpha (1 - \Delta E/RT)$

so Claridge's (Chap. 8)

$\Delta = \Delta E/2RT$

Easiest to use simple numbers, since populations are ~ linear.

[following Sanders&Hunter]



Population Description for Protons

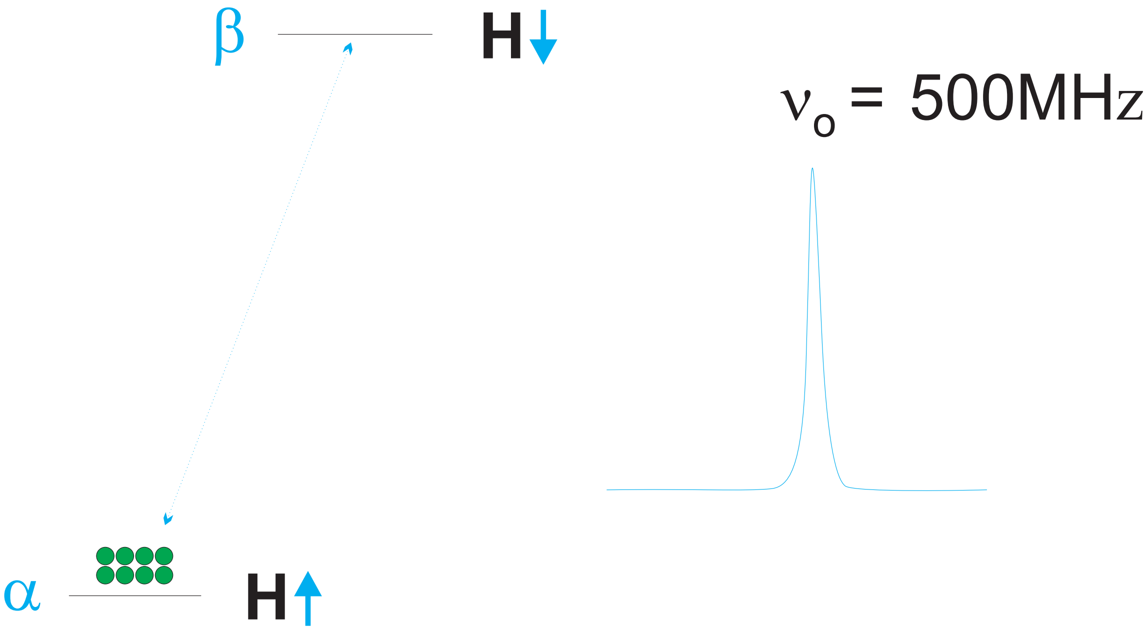
Since $\Delta E/RT \ll 1$

Easiest to use simple numbers, since populations are ~ linear.

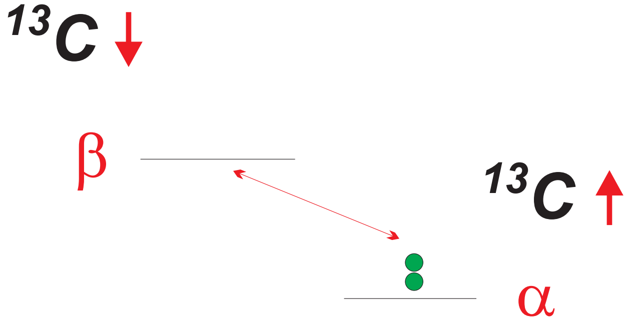
The figure is qualitatively correct, or precisely for 80,000 protons.

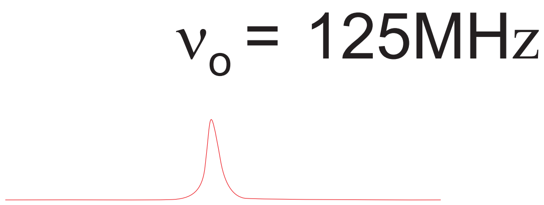
What's shown is the excess population.

[following Sanders&Hunter]



Population Description for ^{13}C





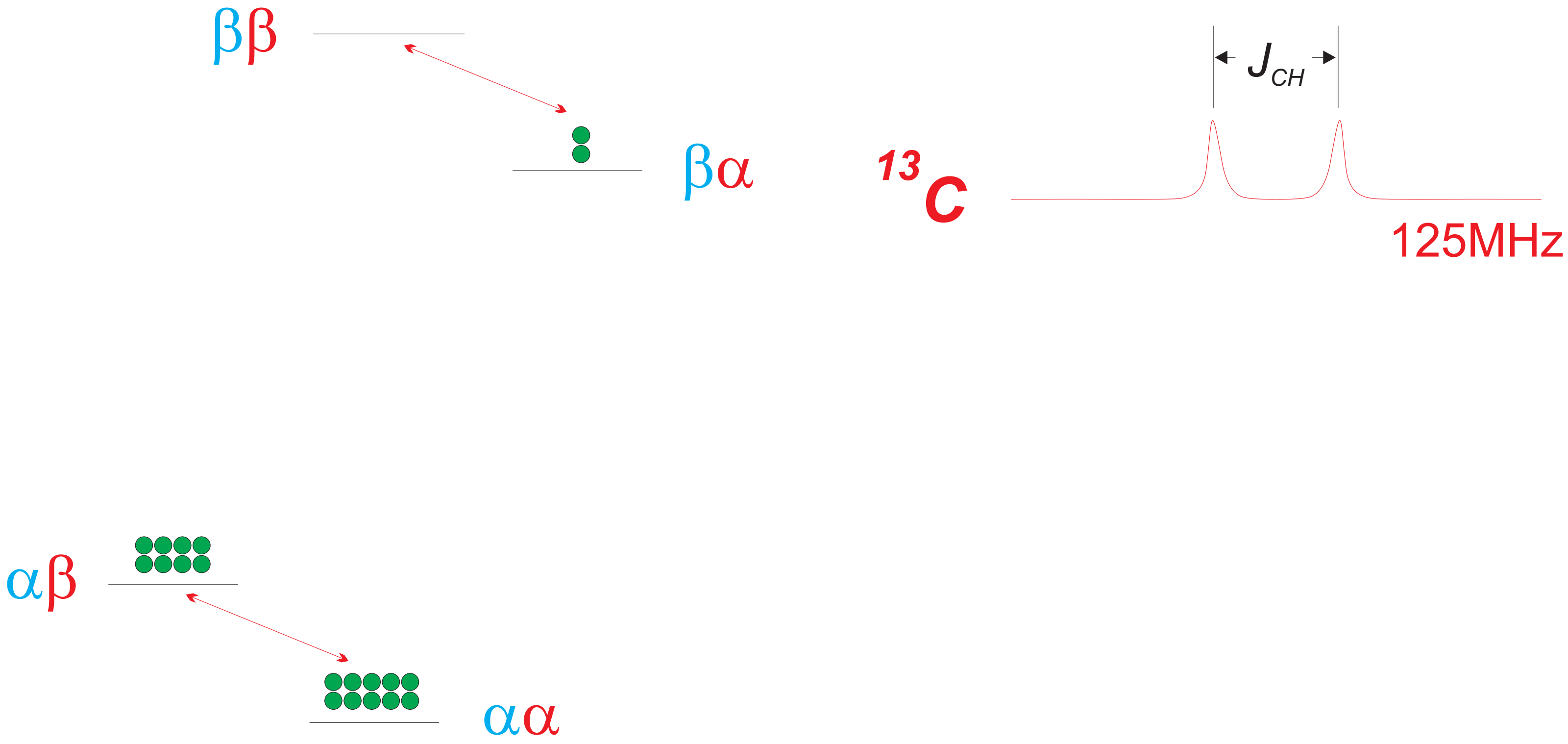
Since

$\gamma_C \sim \gamma_H/4$

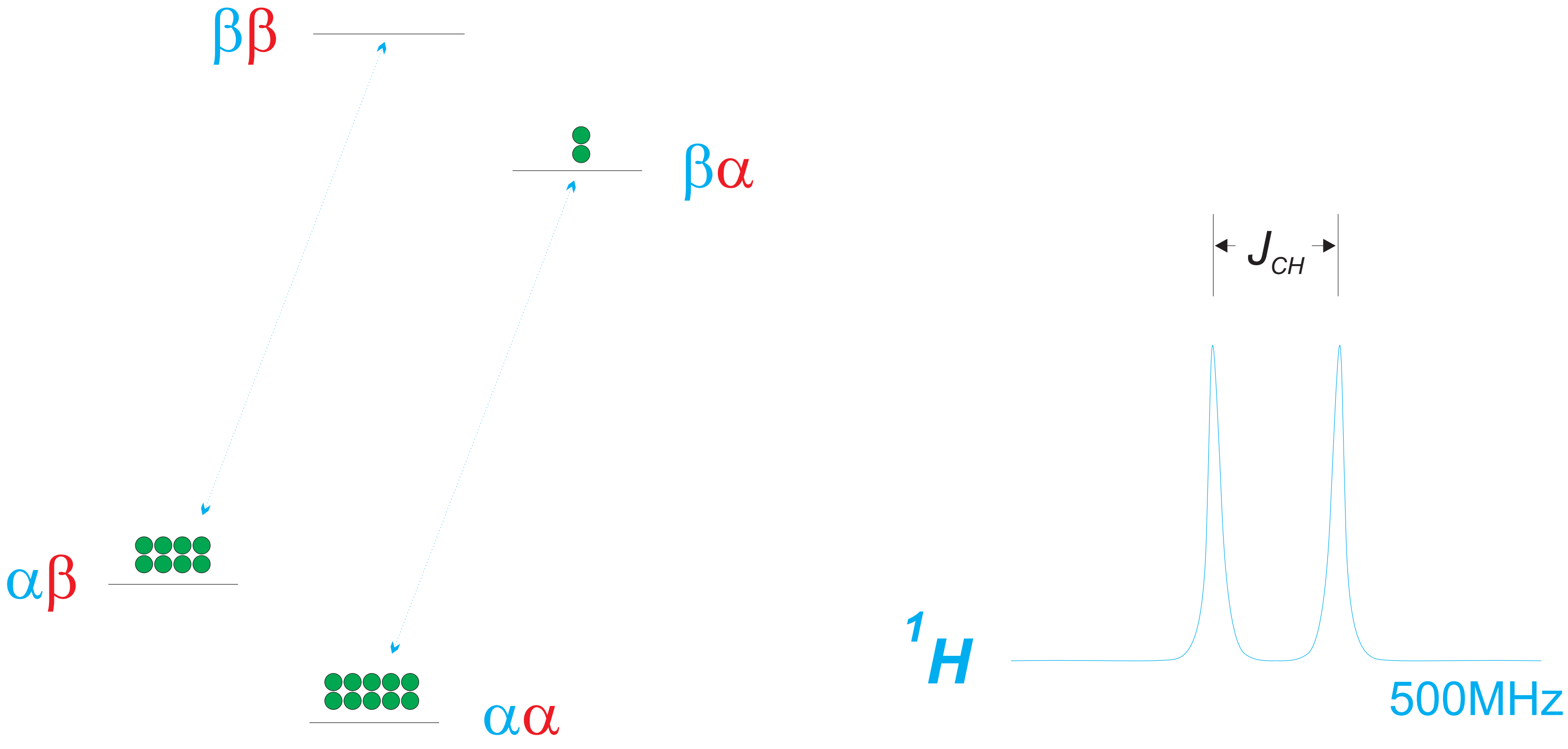
population excess is

1/4th for ^{13}C than for ^{1}H.

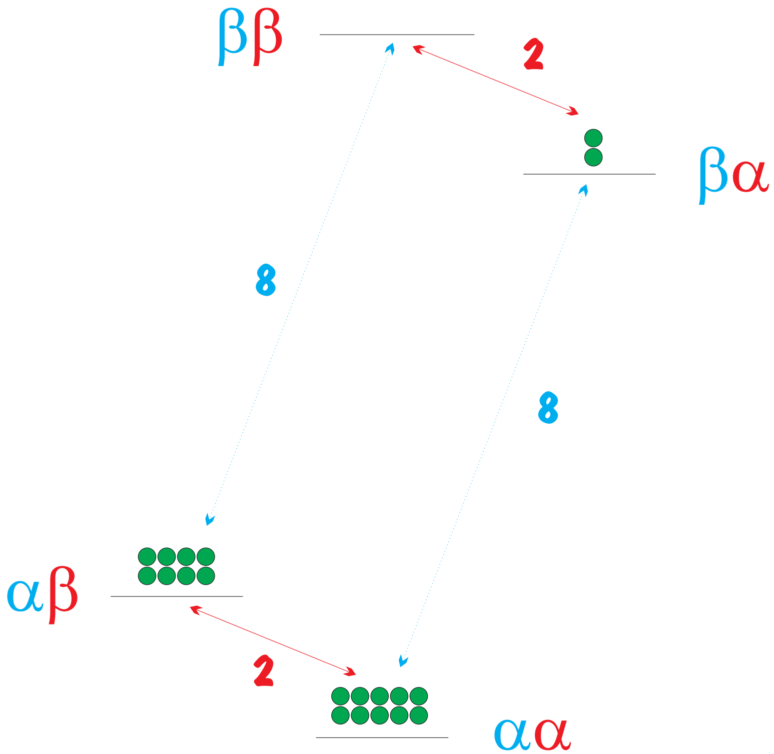
Population Description for Two-Spin Heteronuclear System



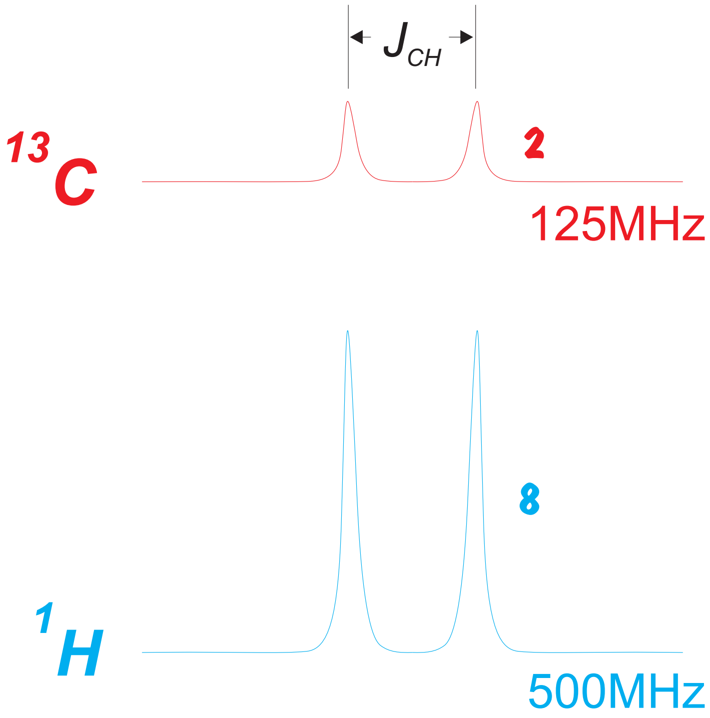
Population Description for Two-Spin Heteronuclear System



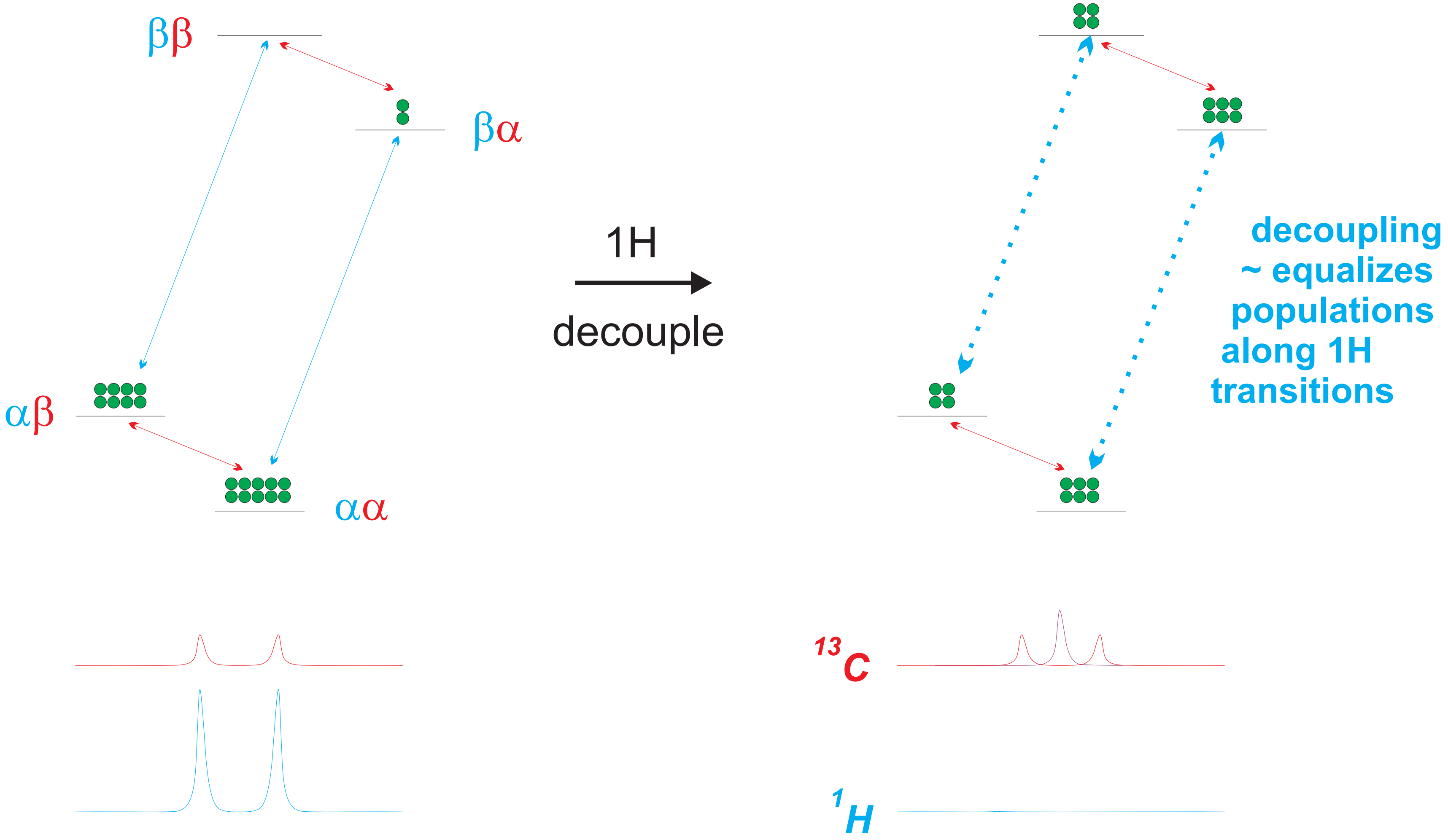
Population Description for Two-Spin Heteronuclear System



Equilibrium Zeeman populations

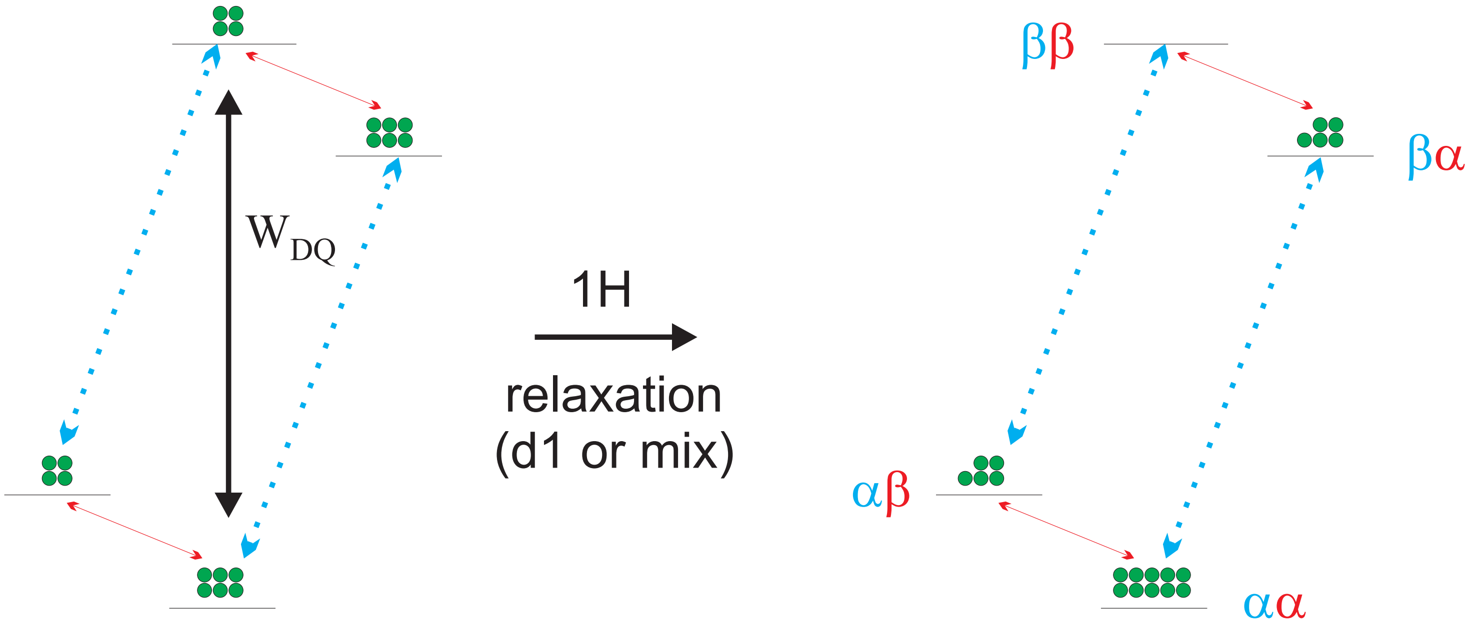


Population Description of Decoupling



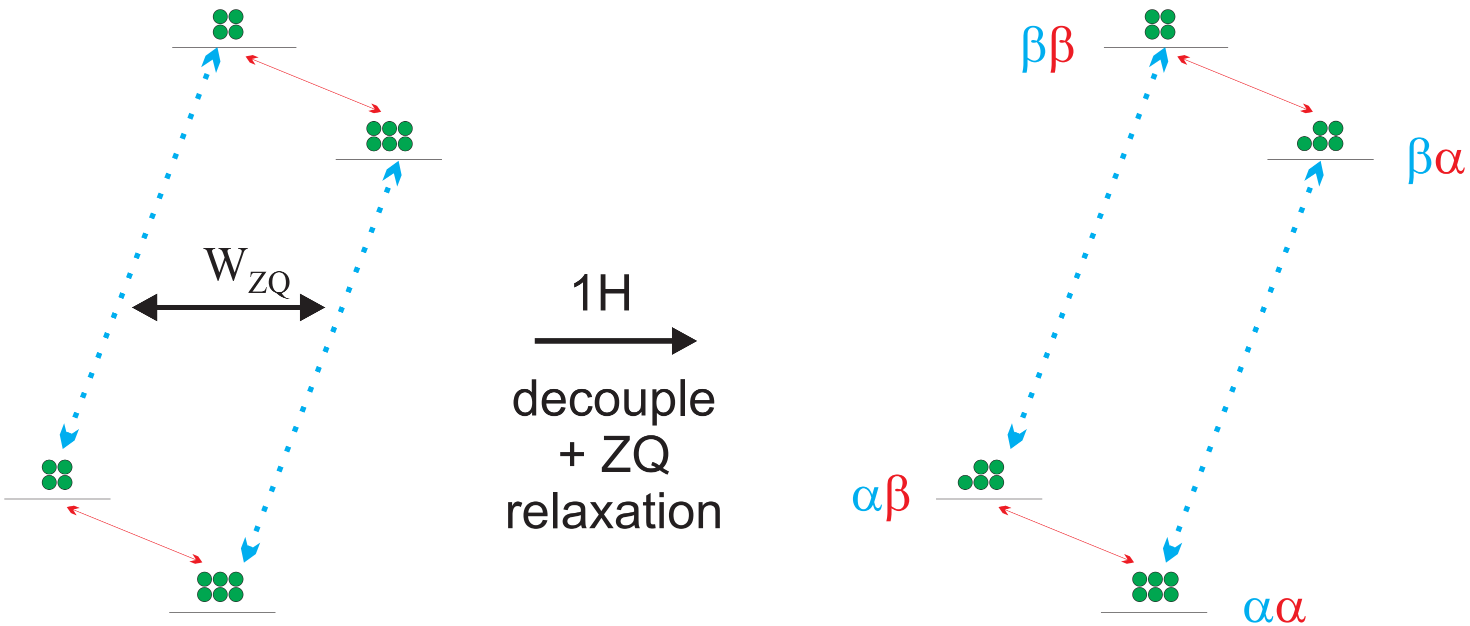
decoupling
~ equalizes
populations
along 1H
transitions

Population Description of NOE



Relaxation will always work to re-establish Zeeman populations. The theory goes beyond this discussion, but hand-waving, we get to something similar to that shown above.

Population Description of NOE

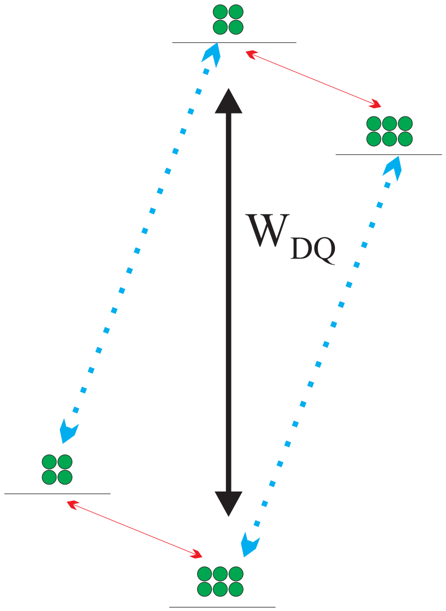


1H

decouple
+ ZQ
relaxation

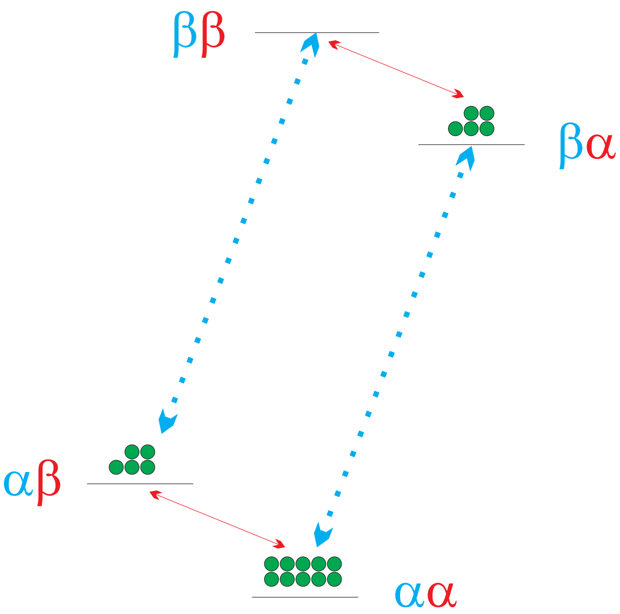
ZQ does not happen in the heteronuclear case with no (ZQ) degenerate energy levels.

Population Description of NOE

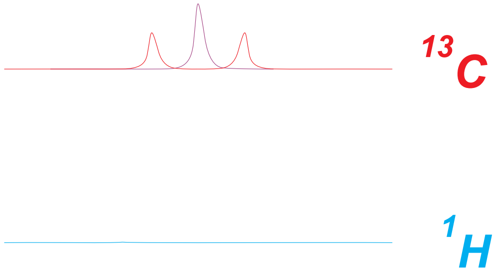


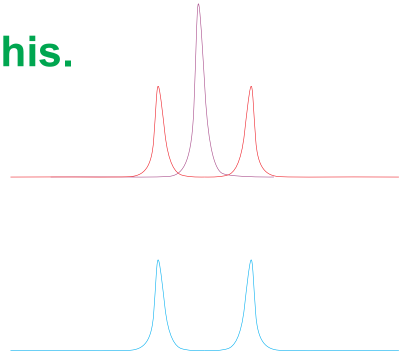
1H →

decouple
+ DQ
relaxation

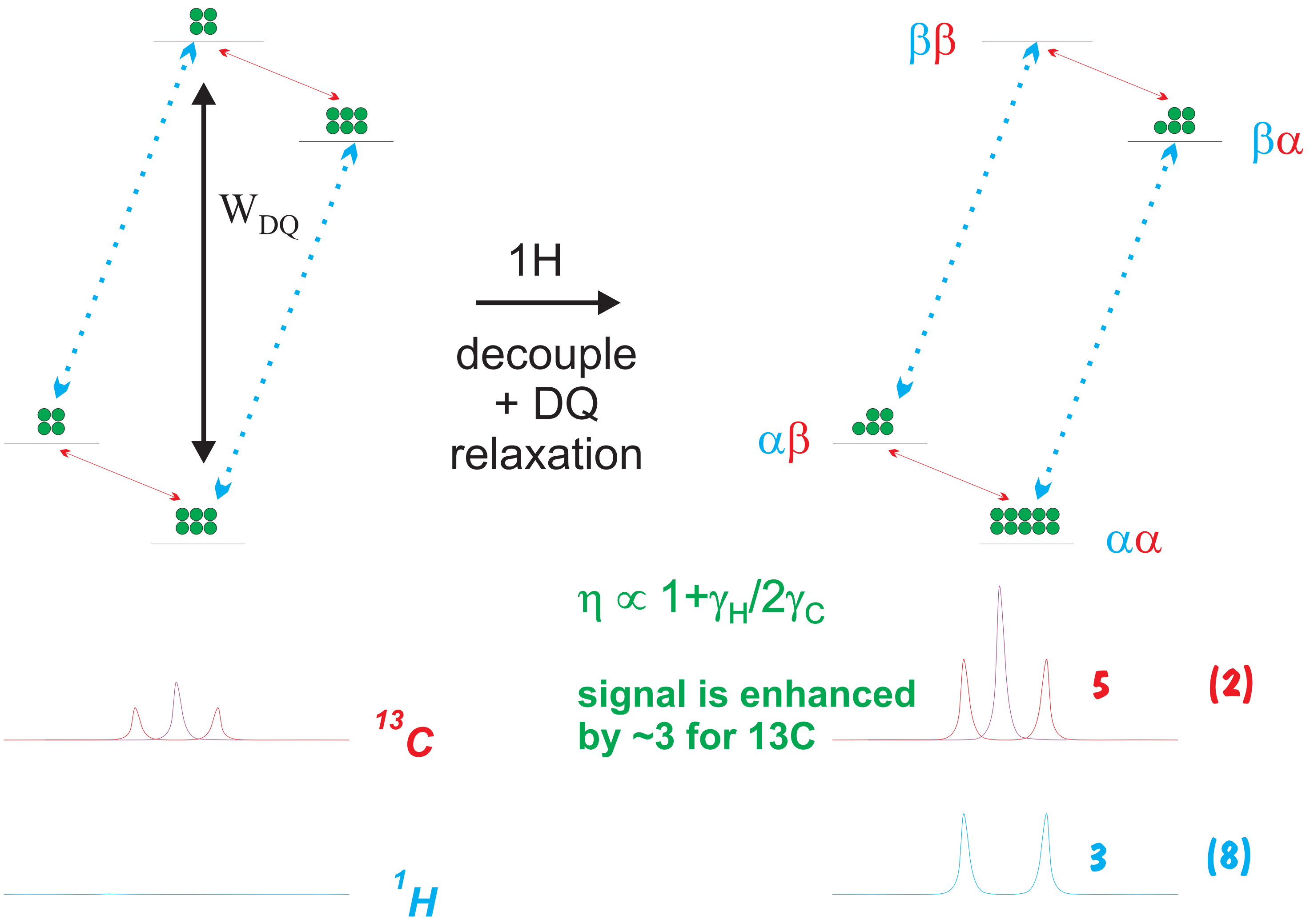


DQ does occur, giving populations something like this.





Population Description of NOE



1H

decouple
+ DQ
relaxation

$\eta \propto 1+\gamma_H/2\gamma_C$

signal is enhanced
by ~3 for 13C

Summary of NOE in Heteronuclear NMR

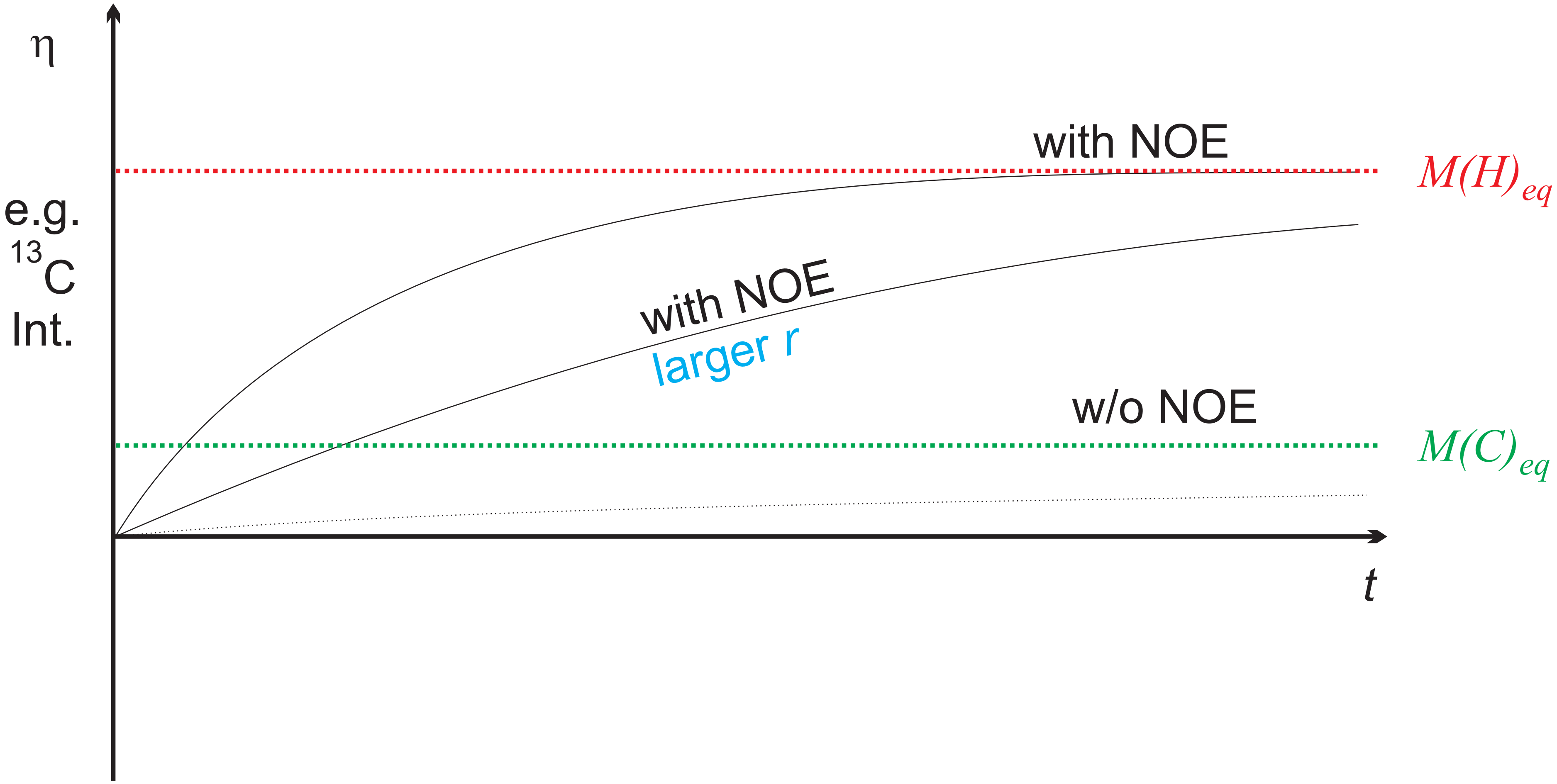
- By far the most common use of NOE in heteronuclear NMR is for signal enhancement. Distance determinations using (**$1/r^6$**) typically are used only in homonuclear (^{1}H-^{1}H) NMR (but see Claridge section 8.9.2).
- Decoupling is not sufficient to affect X-nucleus intensities alone (requires relaxation, typically a few seconds).
- Energy-dependent relaxation creates NOEs:
  - double quantum relaxation creates positive NOEs (positive γ)
    → dominant in heteronuclear systems
    → low MW (small τ_c) in homonuclear systems
  - zero-quantum relaxation creates negative NOEs
    → high MW (large τ_c) in homonuclear systems
- The enhancement maximizes at $1 + \gamma_H/2\gamma_X$. **Note lack of r dependence!!**

1H → 1.5 13C → 3 15N → 4

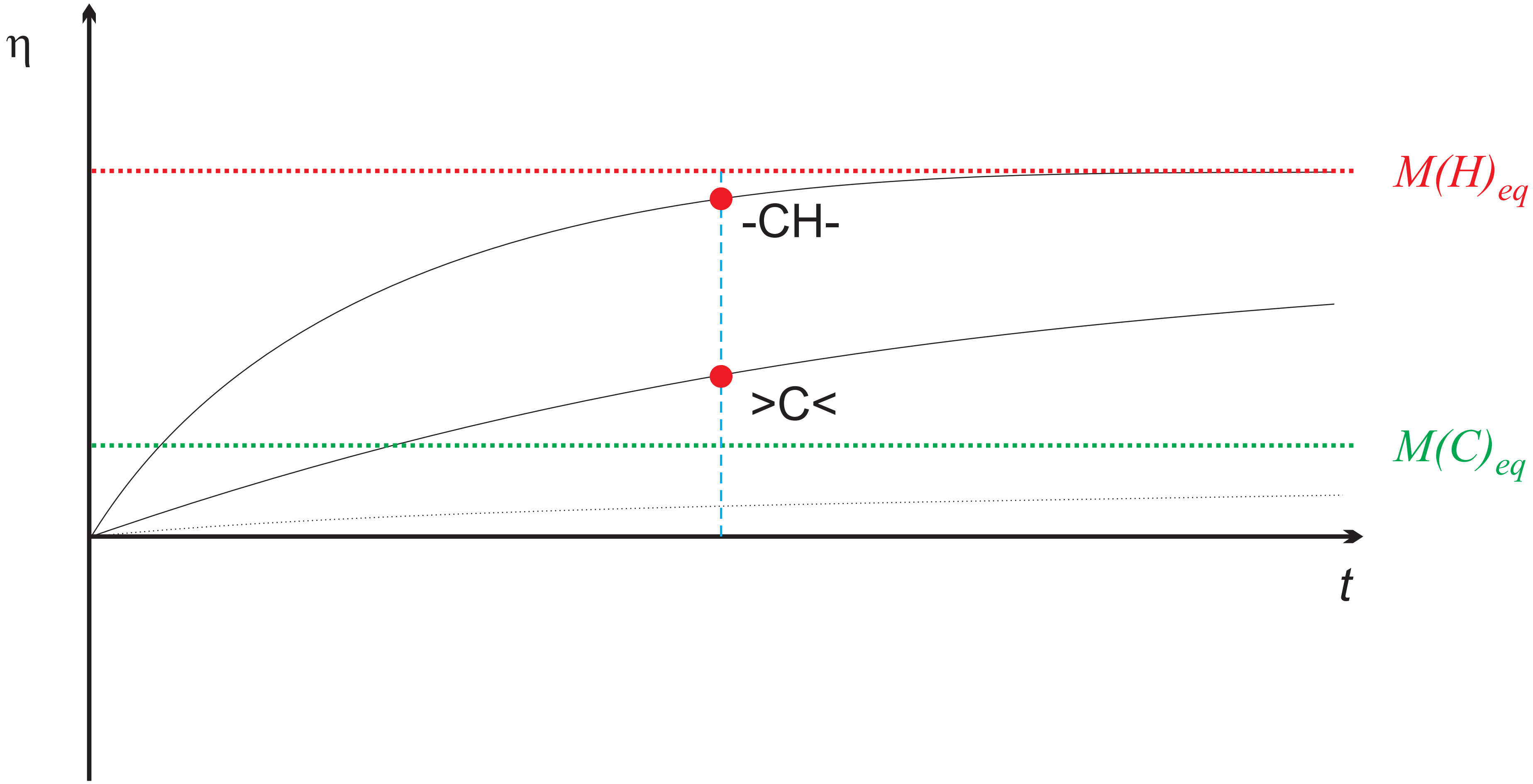
The X-nucleus enhancements are significantly larger for polarization transfer, but a J-coupling must then be present.

Note: enhancement can go to zero for negative γ_X **Use INEPTRD for 29Si!**

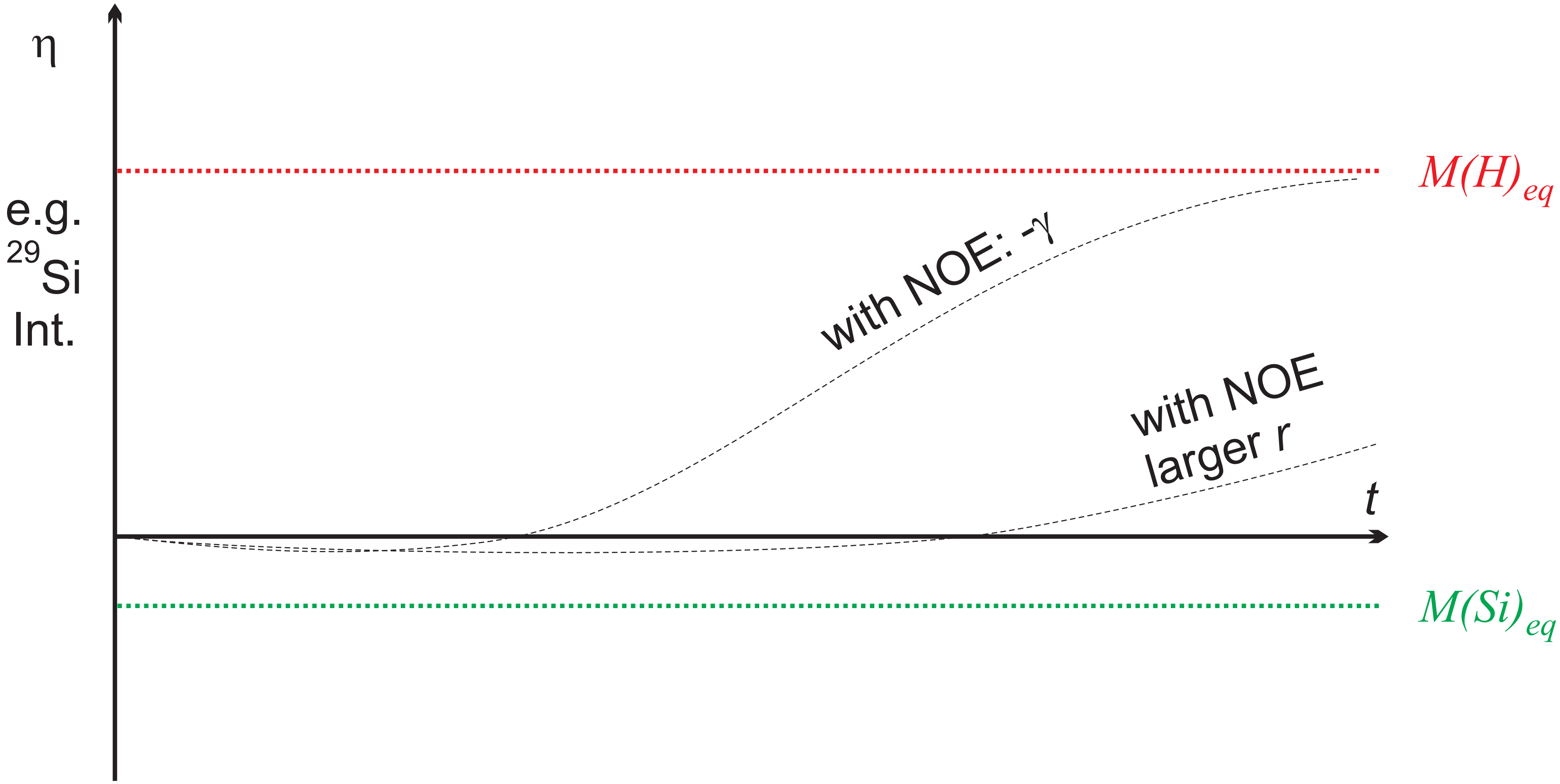
NOE Growth for Positive γ Nuclei



Heteronuclear NOEs: Positive γ Nuclei



NOE Growth for Negative γ Nuclei



Heteronuclear NOEs: Negative γ Nuclei

^{29}Si, ^{15}N, ^{119}Sn