

Chem 440/740
Winter 2010

INTRODUCTION TO NMR and NMR QIP

J. Baugh

Books (NMR):

Spin dynamics: basics of nuclear magnetic resonance, M. H. Levitt, Wiley, 2001.

The principles of nuclear magnetism, A. Abragam, Oxford, 1961.

Principles of magnetic resonance, C. P. Slichter, Springer, 1990.

Reviews (NMR QIP):

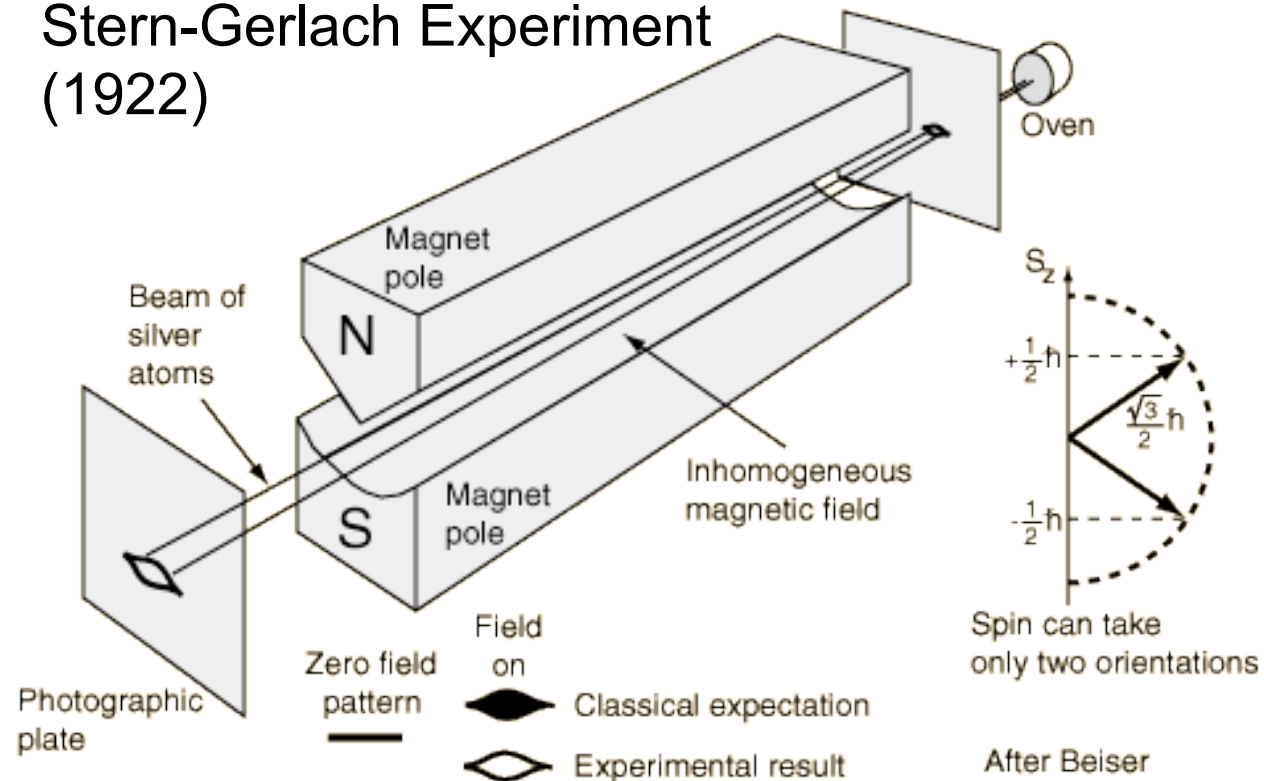
NMR techniques for quantum control and computation, LMK Vandersypen and I. Chuang, *Reviews of Modern Physics* (2004) vol. 76 (4) pp. 1037-1069.

Quantum information processing using nuclear and electron magnetic resonance: review and prospects, J. Baugh et al., 2007. arXiv: 0710.1447.

NMR Based Quantum Information Processing: Achievements and Prospects, D. G. Cory et al., 2000. arXiv:quant-ph/0004104.

What is *Spin*?

Stern-Gerlach Experiment (1922)



$$\boldsymbol{\mu}_s = -\frac{e}{2m} g \mathbf{S}$$

$$S_z = \pm \frac{1}{2} \hbar \quad (s=1/2)$$

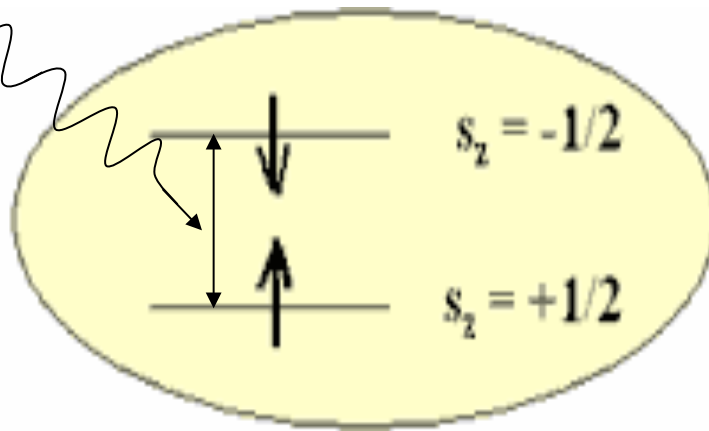
$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B_z$$

$$S = \sqrt{\frac{1}{2}(\frac{1}{2} + 1)} \hbar = \frac{\sqrt{3}}{2} \hbar$$

Zeeman Energy

$$E = -\vec{\mu} \cdot \vec{B} = \mu_z B_z \quad \longrightarrow \quad H = -\mu B_z \cdot \sigma_z / 2 = -\mu B_z \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

$$E = h\nu = \mu B_z$$



$$H|\uparrow\rangle = \frac{-\mu B_z}{2} |\uparrow\rangle$$

$$H|\downarrow\rangle = \frac{+\mu B_z}{2} |\downarrow\rangle$$

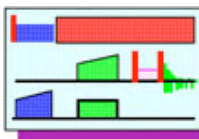
“gyromagnetic ratio”
of isotope n

Electron: $\mu \approx 2\mu_B = \frac{\hbar e}{m}$

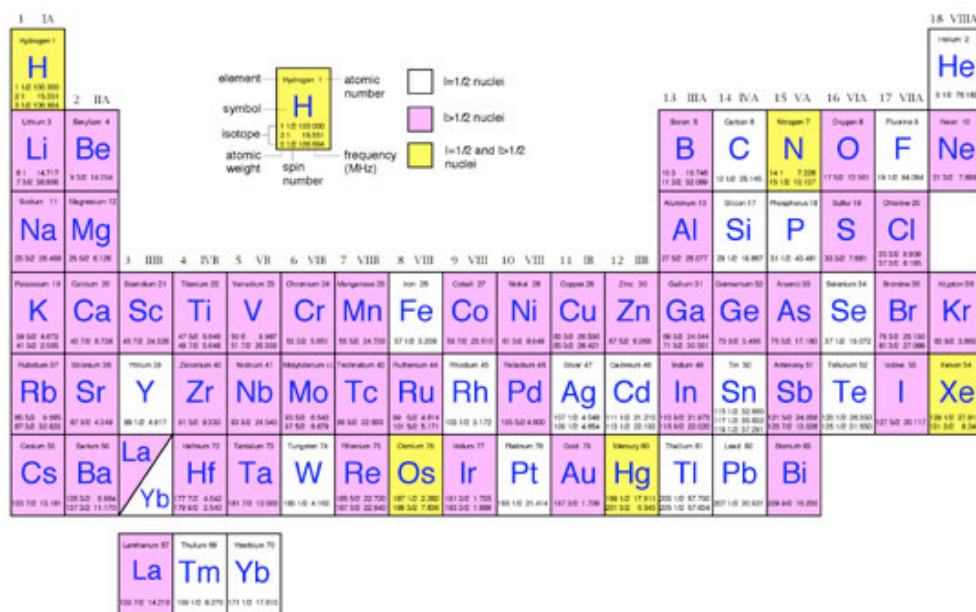
Nucleus: $\mu = \gamma_n$

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Elements Accessible by NMR



Spin-1/2 nucleus	NMR freq (MHz) (at 10 T)	natural abundance
¹ H	426	99.9%
¹³ C	107	1.1%
¹⁵ N	43	0.4%
¹⁹ F	401	100%
²⁸ Si	85	4.7%
³¹ P	175	100%

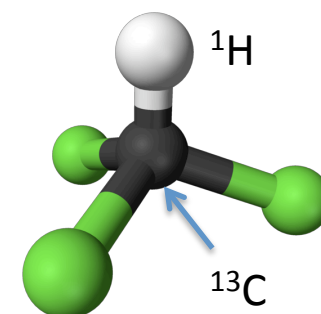
Nuclei with an odd (even) number of nucleons possess half-integer (integer) spin

Nuclei with an even number of protons and neutrons are spinless

NMR Hamiltonian:

2 coupled spins in liquid-state NMR (e.g. ^{13}C -labelled Chloroform)

$$(\hbar = 1) \quad H_0 = \frac{1}{2} (\omega_1 \sigma_{1z} + \omega_2 \sigma_{2z} + \pi J_{12} \sigma_{1z} \sigma_{2z})$$



Chloroform molecule,
 CHCl_3

Larmor frequency (rad/s): $\omega_k = -\gamma_k B$

External magnetic field (T): B

Coupling strength (Hz): J_{kl}

Chemical shielding:

For the same isotope, $\gamma_j = \gamma_0 (1 - \delta_j)$

for nucleus at the j^{th} chemical site.



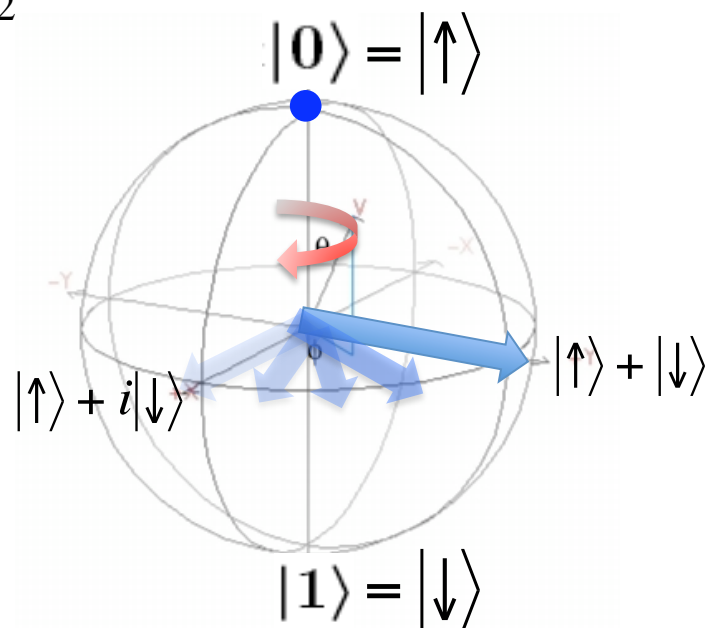
*Ability to address different
nuclei as qubits*

Larmor precession of a single spin

$$H_0 = \frac{\omega_1 \sigma_{1z}}{2} \quad \longrightarrow \quad U(t) = e^{-i\omega_1 t \sigma_{1z} / 2}$$

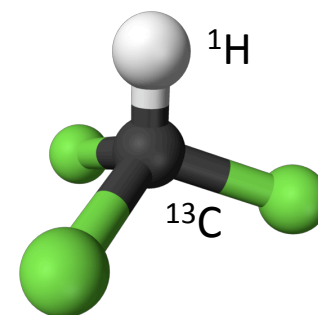
Take $|\psi\rangle = \frac{|\uparrow\rangle + |\downarrow\rangle}{\sqrt{2}}$

$$\begin{aligned} U(t)|\psi\rangle &= \frac{e^{-i\omega_1 t/2}|\uparrow\rangle + e^{+i\omega_1 t/2}|\downarrow\rangle}{\sqrt{2}} \\ &= e^{-i\omega_1 t/2} \left(\frac{|\uparrow\rangle + e^{+i\omega_1 t}|\downarrow\rangle}{\sqrt{2}} \right) \end{aligned}$$



Eigenstates of the Hamiltonian

$$H_0 = \frac{1}{2} (\omega_1 \sigma_{1z} + \omega_2 \sigma_{2z} + \pi J_{12} \sigma_{1z} \sigma_{2z})$$

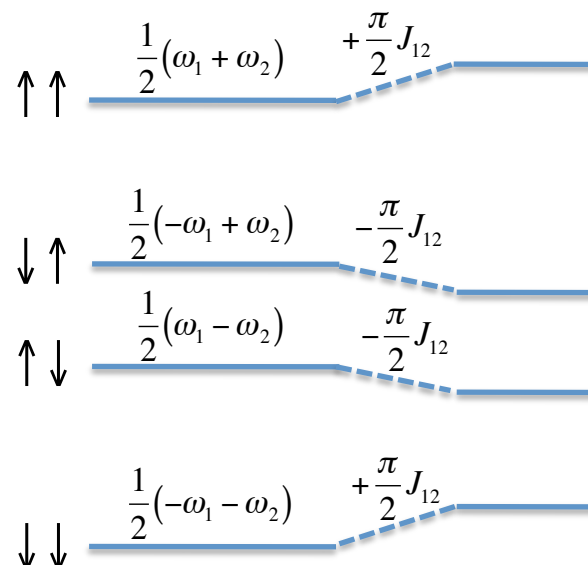


Chloroform molecule,
CHCl₃

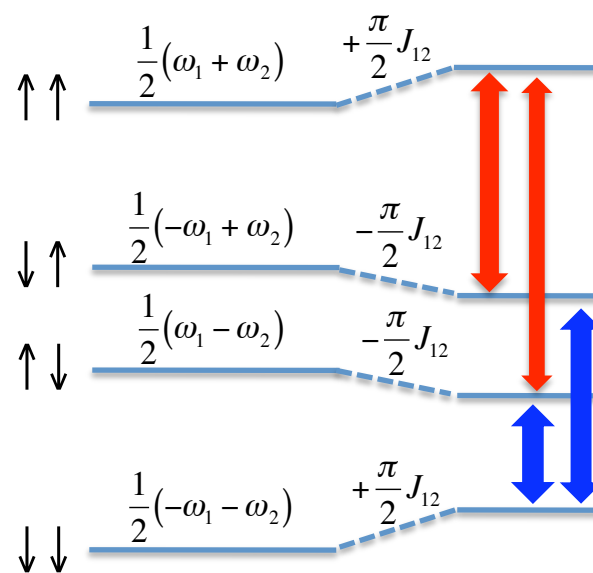
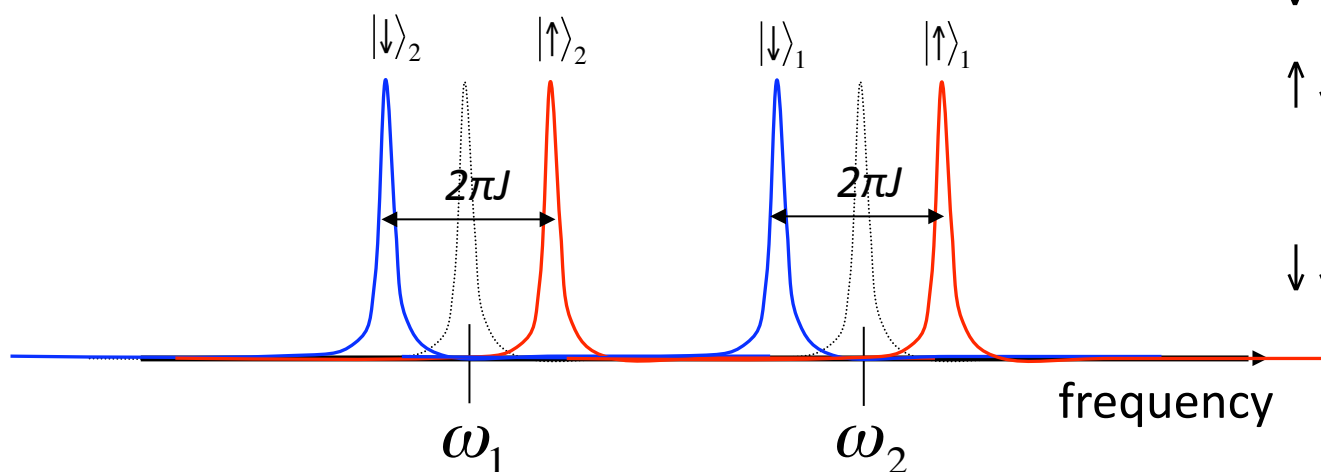
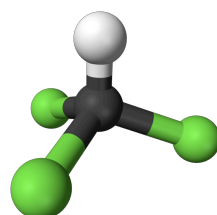
state	eigenvalue
$ \uparrow\uparrow\rangle$	$\frac{1}{2}(\omega_1 + \omega_2 + \pi J_{12})$
$ \downarrow\uparrow\rangle$	$\frac{1}{2}(-\omega_1 + \omega_2 - \pi J_{12})$
$ \uparrow\downarrow\rangle$	$\frac{1}{2}(\omega_1 - \omega_2 - \pi J_{12})$
$ \downarrow\downarrow\rangle$	$\frac{1}{2}(-\omega_1 - \omega_2 + \pi J_{12})$

$$\begin{array}{l}
 1: {}^1\text{H} \quad \omega_1 = 2\pi \times 426 \text{ MHz} \\
 2: {}^{13}\text{C} \quad \omega_2 = 2\pi \times 107 \text{ MHz}
 \end{array}
 \left. \vphantom{\begin{array}{l} 1: {}^1\text{H} \\ 2: {}^{13}\text{C} \end{array}} \right\} B = 10 \text{ T}$$

$$J_{12} \approx 200 \text{ Hz}$$



NMR transitions (spectrum)



These are magnetic dipole transitions, and are thus driven by an oscillating (Radio-frequency, “RF”) magnetic field...

Need transverse spin operators (σ_x, σ_y) to drive them.

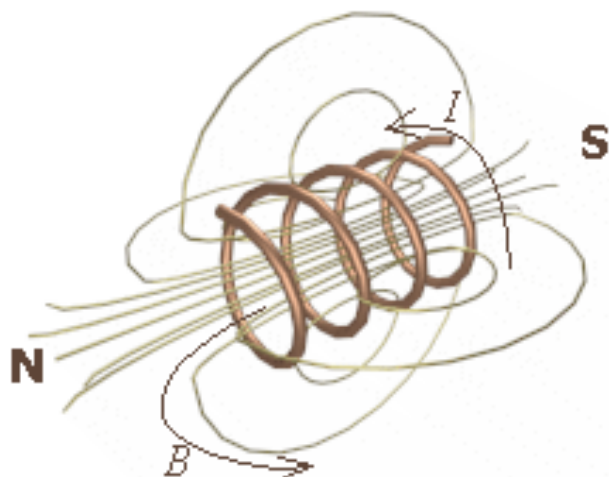
RF Hamiltonian:

$$\theta(t) = \omega_{rf} t + \phi$$

RF frequency

$$H_{rf}(t) = \frac{\Omega(t)}{2} [\sigma_{1x} \cos(\theta(t)) + \sigma_{1y} \sin(\theta(t))]$$

RF amplitude



$$B_x \cos(\omega_{rf} t) = -\omega_{rf} + \omega_{rf}$$

The diagram illustrates the decomposition of a magnetic field component $B_x \cos(\omega_{rf} t)$ into two rotating fields. A vertical double-headed arrow represents the field. This is equal to the sum of two circular fields: one rotating at $-\omega_{rf}$ and one rotating at $+\omega_{rf}$. Each circular field has a central vertical arrow pointing up and a curved arrow indicating the direction of rotation.

**Rotating reference frame transformation:
two isotopes (doubly-rotating frame)**



$$R(t) = e^{i\omega_{1rf}t\sigma_{1z}/2} e^{i\omega_{2rf}t\sigma_{2z}/2}$$

$$|\psi_R\rangle = R(t)|\psi_{lab}\rangle$$

$$\frac{id|\psi_{lab}\rangle}{dt} = H_{lab}|\psi_{lab}\rangle \quad \longrightarrow \quad \frac{id|\psi_R\rangle}{dt} = H_R|\psi_R\rangle$$

$$H_{lab} = H_0 + H_{rf}(t)$$



$$H_R = \frac{1}{2} \left[(\omega_1 - \omega_{1rf})\sigma_{1z} + (\omega_2 - \omega_{2rf})\sigma_{2z} + \pi J_{12}\sigma_{1z}\sigma_{2z} \right] \\ + \frac{1}{2} \left[\Omega_1(t)(\sigma_{1x} \cos(\phi_1) + \sigma_{1y} \sin(\phi_1)) \right] \\ + \frac{1}{2} \left[\Omega_2(t)(\sigma_{2x} \cos(\phi_2) + \sigma_{2y} \sin(\phi_2)) \right]$$

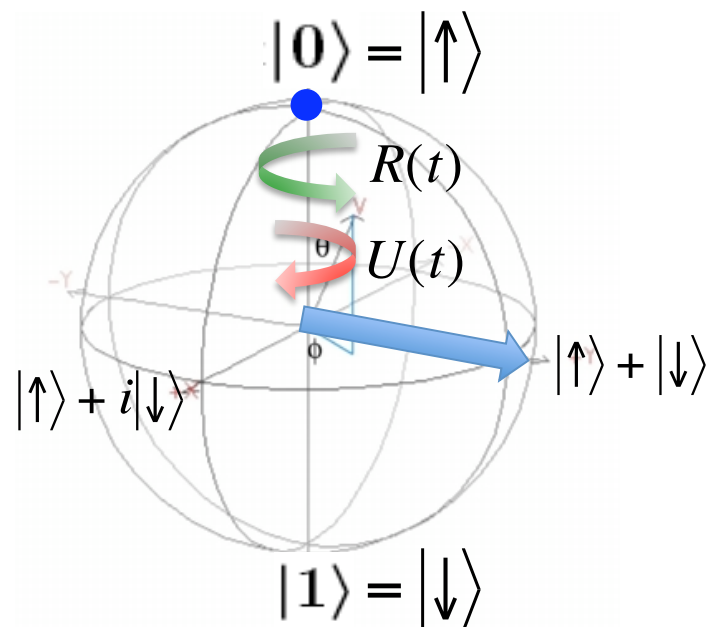
Rotating frame

We had Larmor precession in Lab frame:

$$U(t)|\psi_{Lab}\rangle = e^{-i\omega_1 t/2} \left(\frac{|\uparrow\rangle + e^{+i\omega_1 t}|\downarrow\rangle}{\sqrt{2}} \right)$$

But in the rotating frame (on resonance):

$$R(t)|\psi_{Lab}(t)\rangle = R(t)(U(t)|\psi_{Lab}\rangle) = \frac{|\uparrow\rangle + |\downarrow\rangle}{\sqrt{2}}$$



Resonant pulses as Bloch sphere rotations

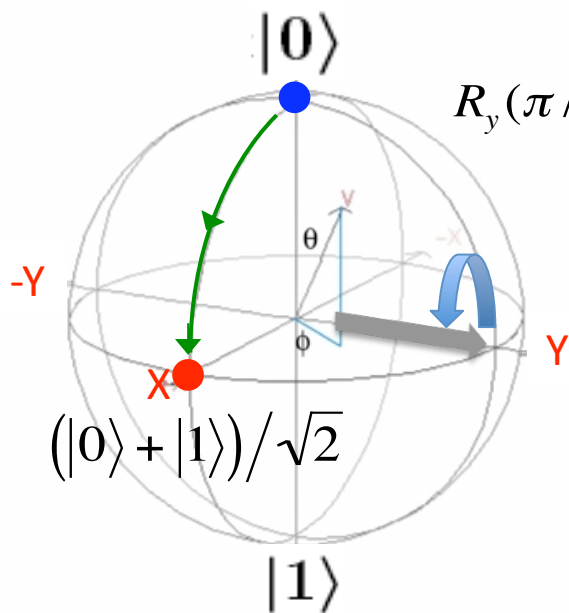
Consider a single spin at resonance:

$$H_R = \frac{1}{2} \left[(\omega_1 - \omega_{1rf}) \sigma_{1z} + \Omega_1(t) (\sigma_{1x} \cos(\phi_1) + \sigma_{1y} \sin(\phi_1)) \right]$$

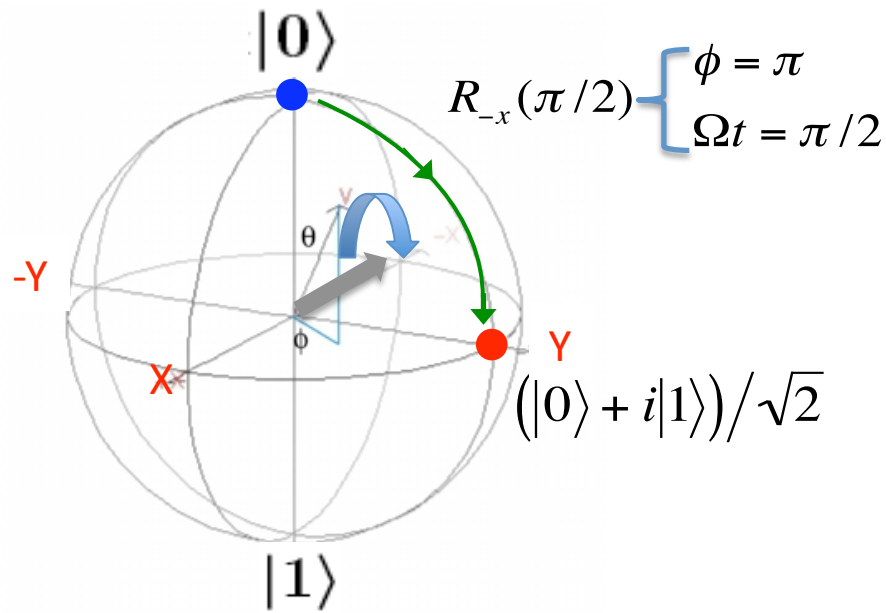
$\omega_1 = \omega_{1rf}$

$$U(t) = e^{-i\Omega_1 t (\sigma_{1x} \cos(\phi_1) + \sigma_{1y} \sin(\phi_1)) / 2}$$

In NMR, we can control both RF phase (ϕ) and amplitude (Ω) in time, so we can perform arbitrary single spin rotations...

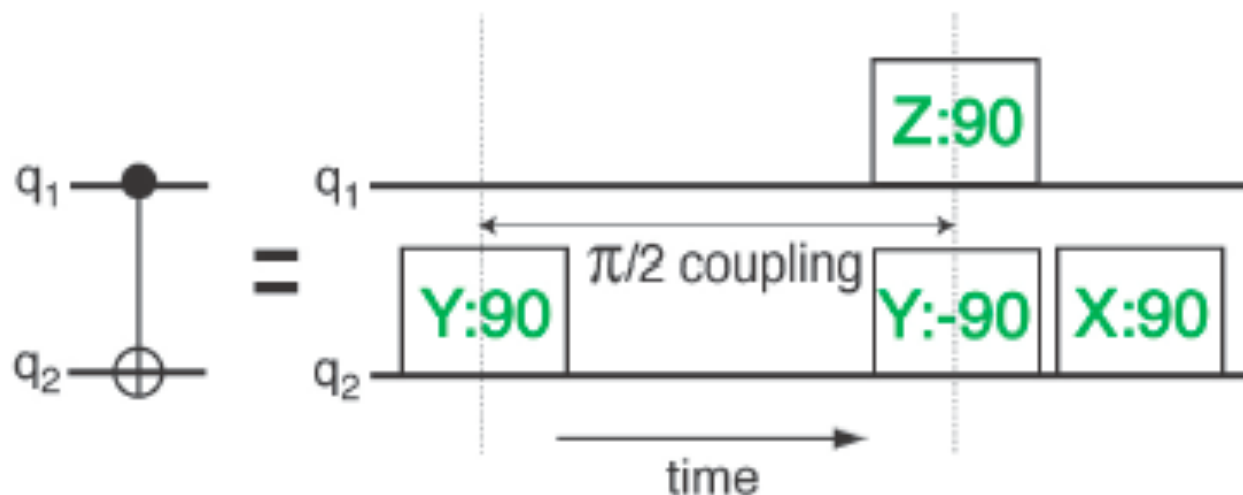


$$R_y(\pi/2) \begin{cases} \phi = \pi/2 \\ \Omega t = \pi/2 \end{cases}$$

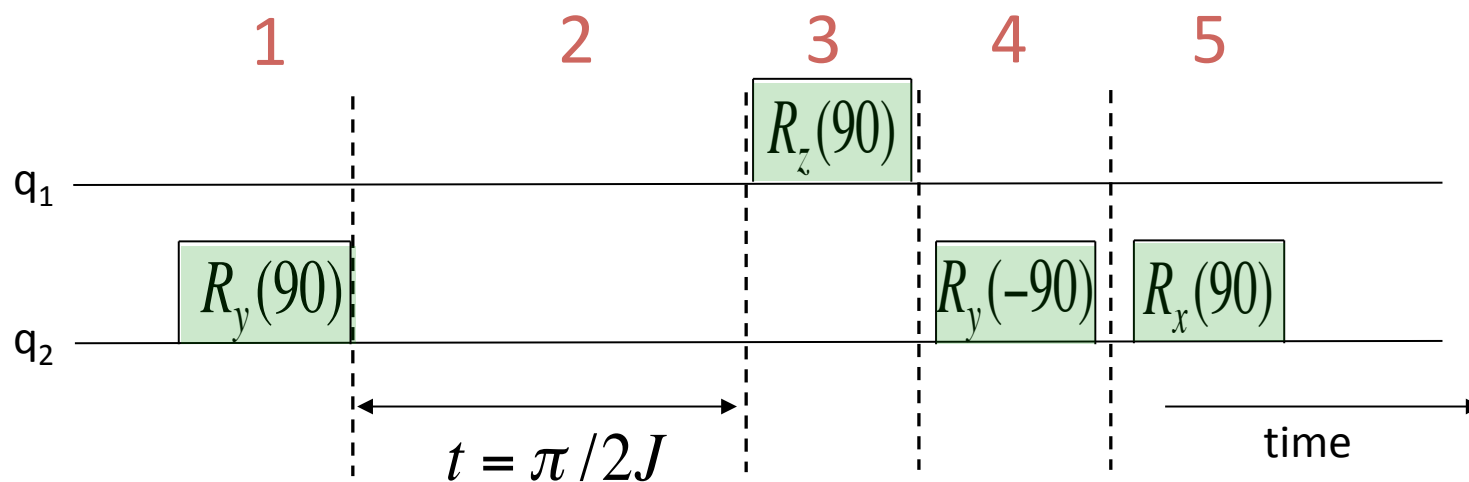


$$R_{-x}(\pi/2) \begin{cases} \phi = \pi \\ \Omega t = \pi/2 \end{cases}$$

Example of two-qubit logic: the CNOT gate



$$H(t) = \frac{1}{2} \left(\underbrace{\omega_1 \sigma_{1z} + \omega_2 \sigma_{2z}}_{\text{Zeeman}} + \underbrace{\pi J \sigma_{1z} \sigma_{2z}}_{\text{coupling}} \right) + \underbrace{H_{rf}(t)}_{\text{RF pulses (control)}}$$



$$U_1 = e^{-i\frac{\pi}{2}I_1 \otimes \frac{\sigma_{1y}}{2}}$$

$$U_2 = e^{-i\frac{\pi}{2}\sigma_{1z} \otimes \sigma_{2z}/2}$$

$$U_3 = e^{-i\frac{\pi}{2}\frac{\sigma_{1z}}{2} \otimes I_2}$$

$$U_4 = e^{+i\frac{\pi}{2}I_1 \otimes \frac{\sigma_{2y}}{2}}$$

$$U_5 = e^{-i\frac{\pi}{2}I_1 \otimes \frac{\sigma_{2x}}{2}}$$

$$U_{CNOT} = U_5 U_4 U_3 U_2 U_1$$

$$= |0\rangle\langle 0|_1 \otimes I_2 + |1\rangle\langle 1|_1 \otimes \sigma_{2x}$$

The thermal state

A general mixed state: $\rho = \sum_k a_k |\psi_k\rangle\langle\psi_k|$

Thermal equilibrium
(Boltzmann distribution): $\rho_{th} = \frac{e^{-H_0/kT}}{\text{Tr}(e^{-H_0/kT})}$

In the high temperature limit ($|H_0| \ll kT$)

$$\rho_{th} \approx \frac{1}{2} \left(\mathbf{I} - \frac{H_0}{kT} \right) \approx \frac{\mathbf{I}}{2} - \frac{1}{4kT} (\omega_1 \sigma_{1z} + \omega_2 \sigma_{2z}) \quad (\text{two-spin case})$$

$\hbar\omega/kT \sim 10^{-5}$ at room temperature in NMR

The thermal state

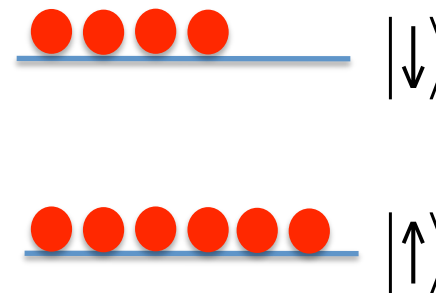
$$\rho_{th} \approx \frac{1}{2} \left(\mathbf{I} - \frac{H_0}{kT} \right) \approx \frac{\mathbf{I}}{2} - \frac{1}{4kT} (\omega_1 \sigma_{1z} + \omega_2 \sigma_{2z})$$

The identity term cannot be changed by pulses or observed...

So we define a 'deviation' density matrix (note it is not a "proper" density matrix, since $Tr(\rho) \neq 1$)

$$\rho_{dev} = \frac{H_0}{kT} \propto \omega_1 \sigma_{1z} + \omega_2 \sigma_{2z} \quad (\text{the J coupling term is } \sim 10^{-6} \text{ times smaller than Zeeman energy})$$

σ_z indicates a population difference
between spin-up and spin-down states



Pseudopure states

To initialize an NMR quantum info. processor, we want a pure state...or at least one that behaves like a pure state:

$$\rho_{pp} = \frac{\mathbf{I}}{2} - \alpha|\psi\rangle\langle\psi|$$

Example: making a $^1\text{H} - ^{13}\text{C}$ pseudopure state

$$\rho_{dev} \approx 4\sigma_{1z} + \sigma_{2z} = \begin{pmatrix} 5 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & -5 \end{pmatrix}$$

Example: making a $^1\text{H} - ^{13}\text{C}$ pseudopure state

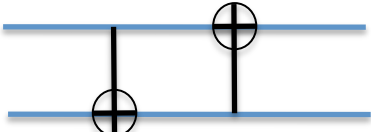
Apply three permutation circuits and sum results:

ρ_{dev}



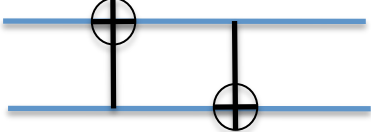
$$\begin{pmatrix} 5 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & -5 \end{pmatrix}$$

ρ_{dev}



$$\begin{pmatrix} 5 & 0 & 0 & 0 \\ 0 & -5 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}$$

ρ_{dev}



$$\begin{pmatrix} 5 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 \\ 0 & 0 & -5 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}$$

$$\Sigma \rightarrow \begin{pmatrix} 15 & 0 & 0 & 0 \\ 0 & -5 & 0 & 0 \\ 0 & 0 & -5 & 0 \\ 0 & 0 & 0 & -5 \end{pmatrix} = 20 \cdot |00\rangle\langle 00| - 5 \cdot I$$

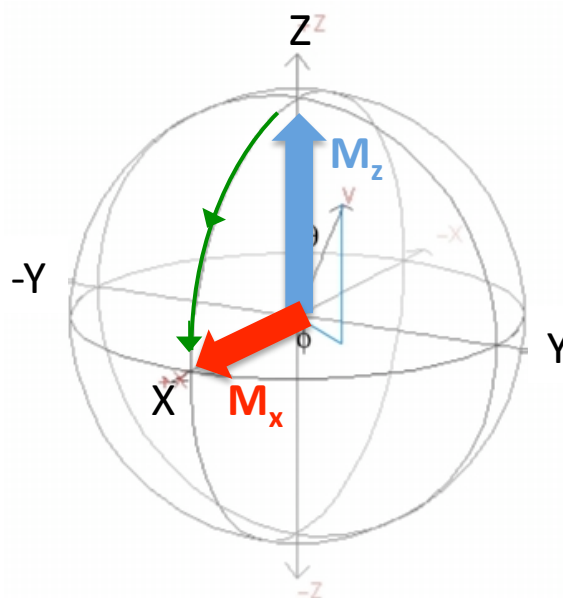
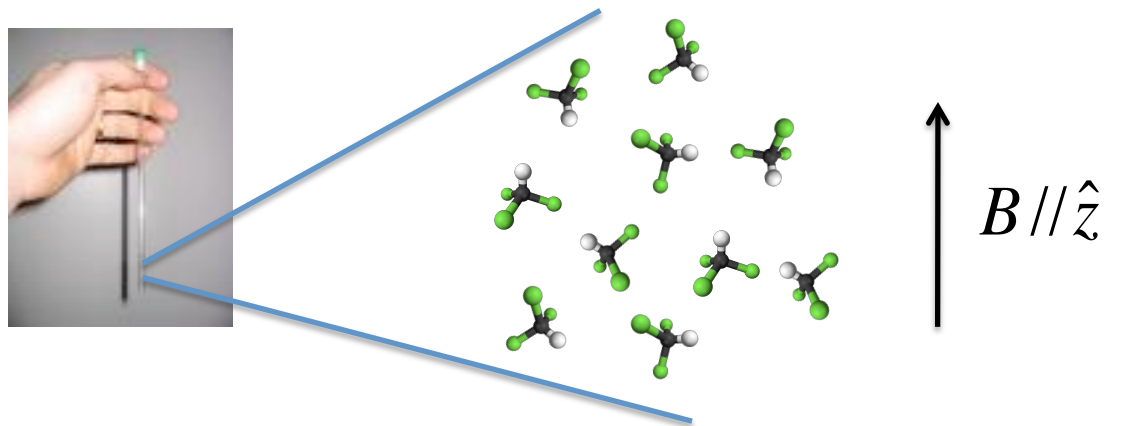
$\rightarrow \rho'_{dev} \propto |00\rangle\langle 00|$

Measurement in NMR

Bulk magnetization of j^{th}
isotope:

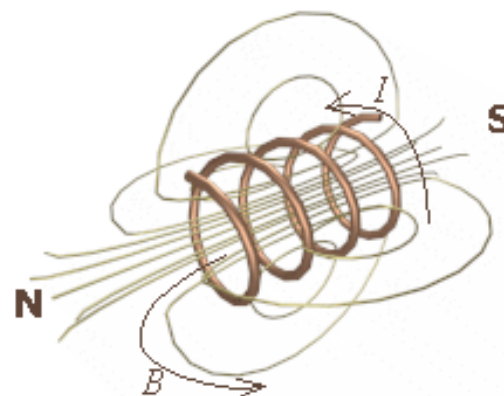
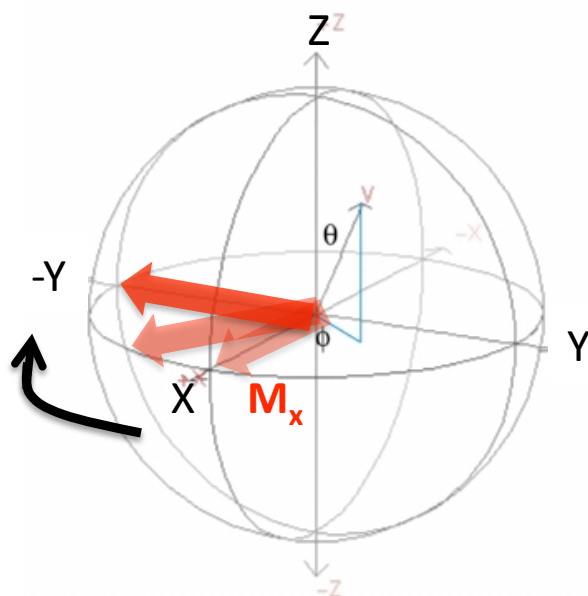
$$M_z^j = \mu_j \cdot (n_{j\uparrow} - n_{j\downarrow})$$

90 degree ("readout") pulse
rotates magnetization to x-y
plane:



Measurement in NMR

In the lab frame, magnetization precesses in the x-y plane, at the Larmor frequency...



...the oscillating magnetic flux induces an emf in the solenoid coil via Faraday's law.

Measurement in NMR

This corresponds to an expectation value measurement,
with observables:

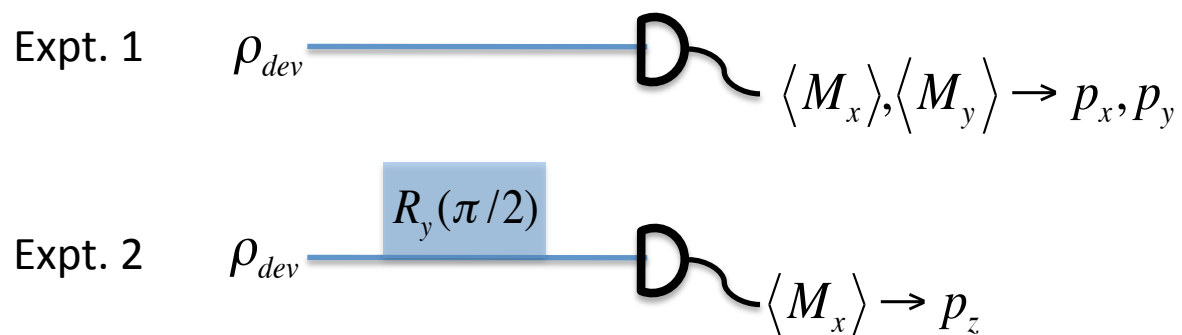
$$\langle M_x \rangle = \text{Tr} \left(\rho \cdot \sum_k \sigma_{x,k} \right) = \text{Tr} \left(\rho_{dev} \cdot \sum_k \sigma_{x,k} \right)$$

$$\langle M_y \rangle = \text{Tr} \left(\rho \cdot \sum_k \sigma_{y,k} \right) = \text{Tr} \left(\rho_{dev} \cdot \sum_k \sigma_{y,k} \right)$$

We call these observables “transverse magnetization”

Measurement in NMR

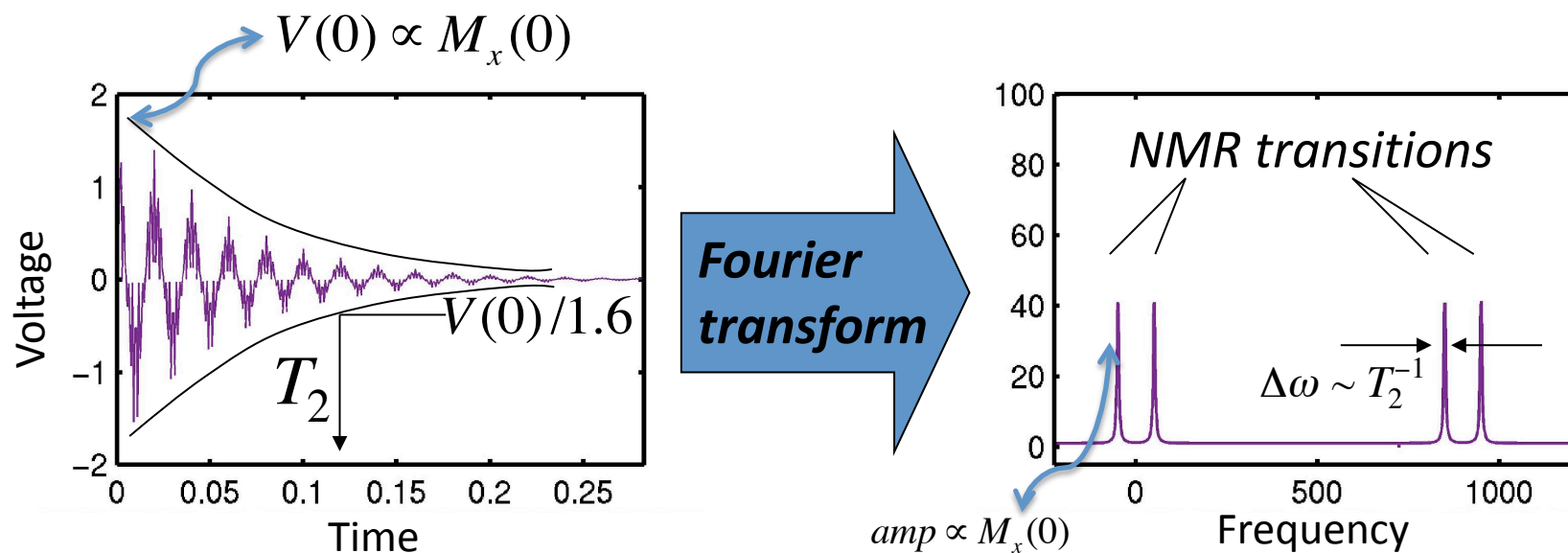
Example: 1-qubit tomography of an arbitrary state ρ_{dev}



$$\rho_{dev} \rightarrow \frac{p_x \sigma_x + p_y \sigma_y + p_z \sigma_z}{\sqrt{p_x^2 + p_y^2 + p_z^2}}$$

Unfortunately, the # of expts needed grows exponentially with # qubits, regardless of the physical system we use for implementation!

Measurement in NMR : FT spectrum



“free-induction signal”

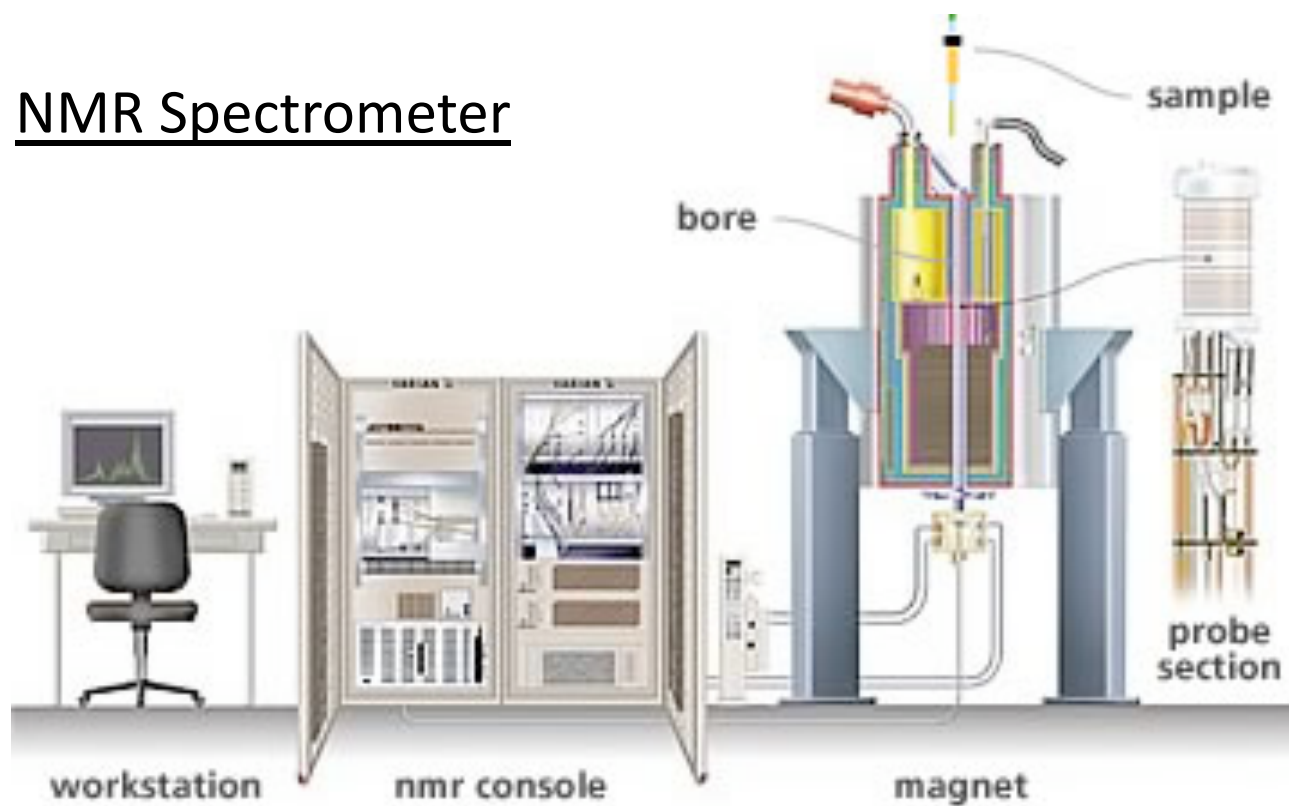
$$M_x(t) = \text{Tr}(\rho(t) \cdot \sigma_x) = \text{Tr}(e^{-iH_0 t} \rho(0) e^{+iH_0 t} \cdot \sigma_x)$$

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NMR Spectrometer



Deutsch-Jozsa Algorithm

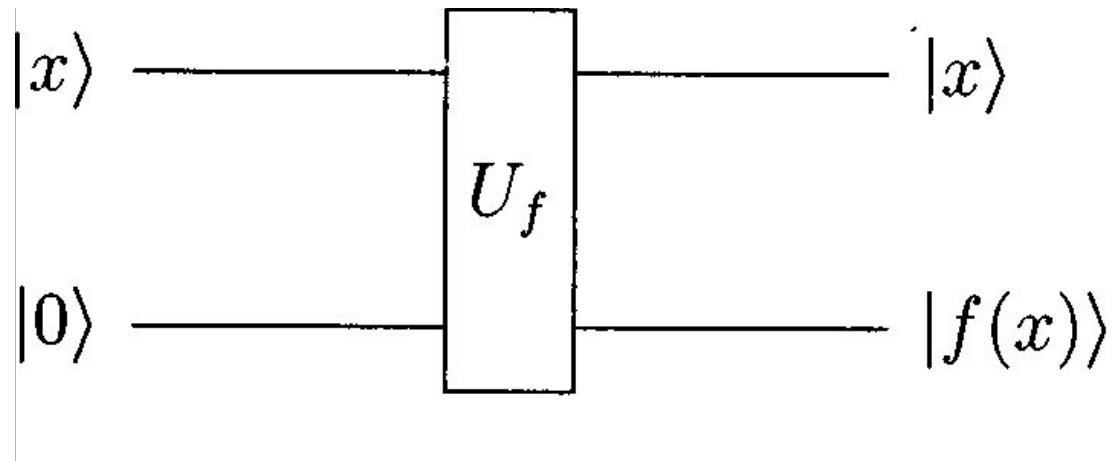
TABLE II. The four possible binary functions mapping one bit to another.

x	$f_{00}(x)$	$f_{01}(x)$	$f_{10}(x)$	$f_{11}(x)$
0	0	0	1	1
1	0	1	0	1

'balanced'

'constant'

Quantum circuit to compute binary function f .



Or another representation:

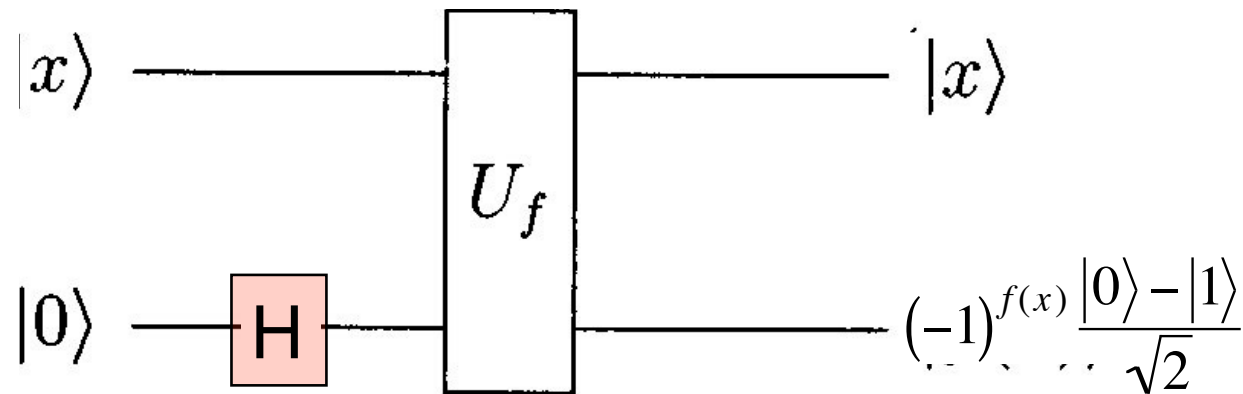
$$|0\rangle|0\rangle \xrightarrow{U_f} |0\rangle|f(0)\rangle$$

and

$$|1\rangle|0\rangle \xrightarrow{U_f} |1\rangle|f(1)\rangle.$$

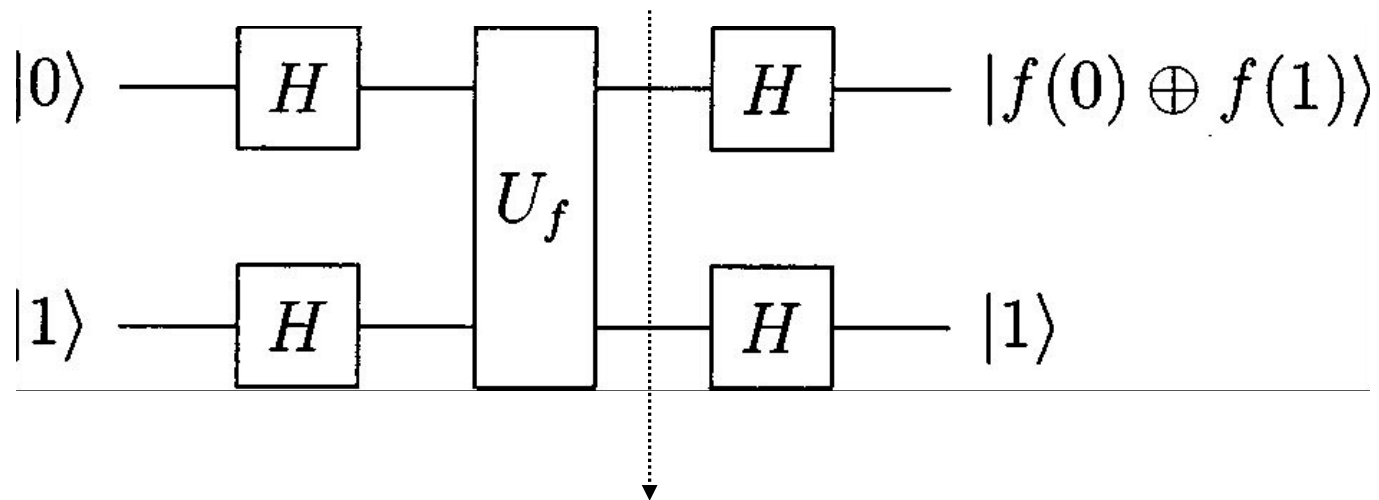
Hadamard gate

$$|0\rangle \xrightarrow{H} \frac{|0\rangle + |1\rangle}{\sqrt{2}}, \quad |1\rangle \xrightarrow{H} \frac{|0\rangle - |1\rangle}{\sqrt{2}}.$$

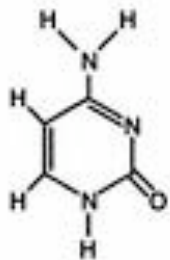


$$|x\rangle \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}} \right) \xrightarrow{U_f} |x\rangle \left(\frac{|0 \oplus f(x)\rangle - |1 \oplus f(x)\rangle}{\sqrt{2}} \right),$$

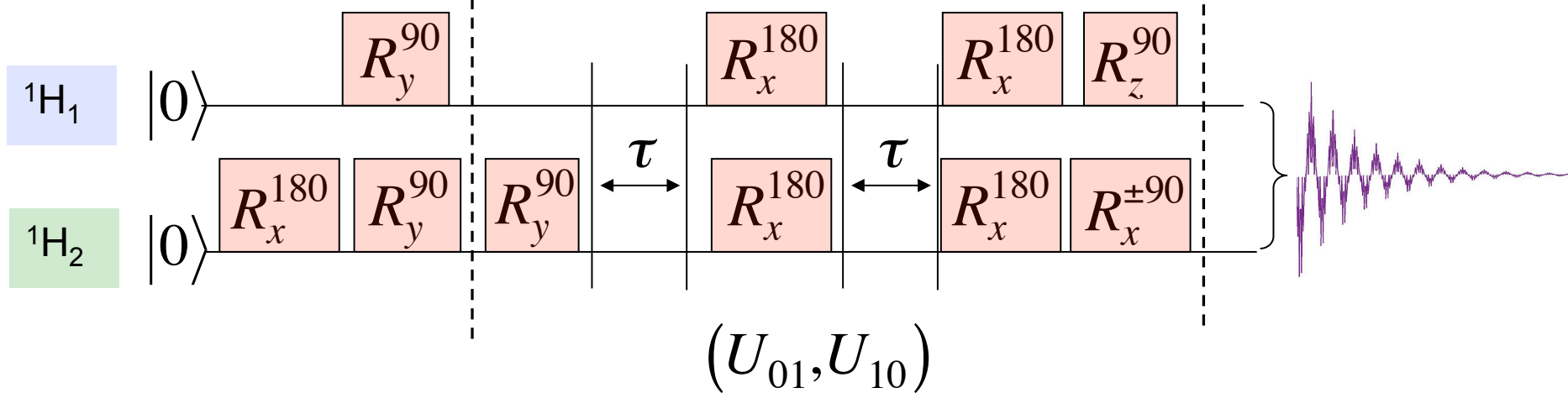
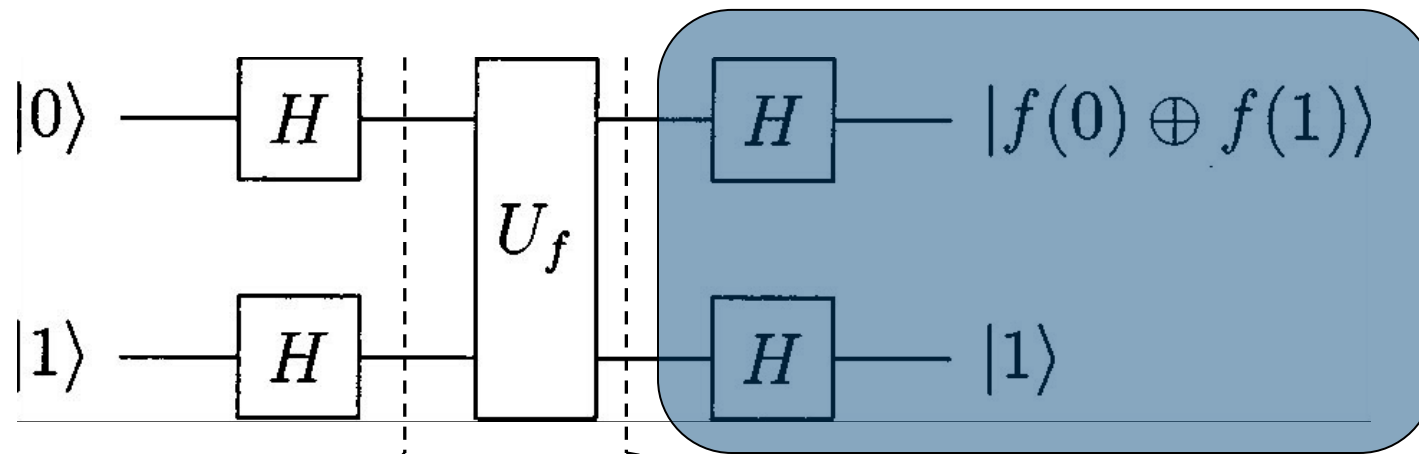
$$= \begin{cases} |x\rangle \frac{|0\rangle - |1\rangle}{\sqrt{2}}, & \text{if } f(x) = 0, \\ |x\rangle \frac{|1\rangle - |0\rangle}{\sqrt{2}}, & \text{if } f(x) = 1, \end{cases} = (-1)^{f(x)} |x\rangle \frac{|0\rangle - |1\rangle}{\sqrt{2}}.$$



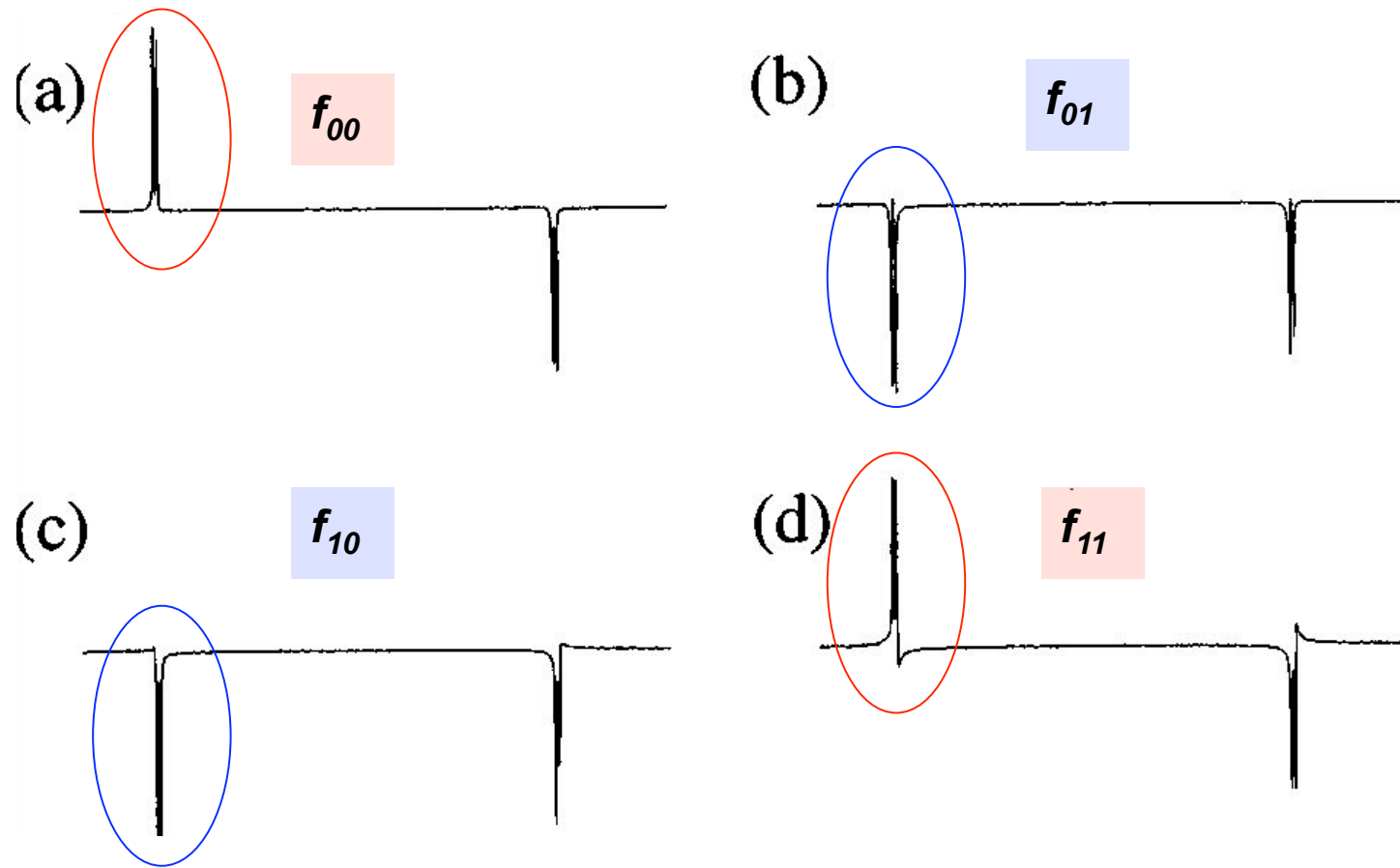
$$\begin{aligned}
 & \left(\frac{|0\rangle + |1\rangle}{\sqrt{2}} \right) \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}} \right) \xrightarrow{U_f} \left(\frac{(-1)^{f(0)}|0\rangle + (-1)^{f(1)}|1\rangle}{\sqrt{2}} \right) \\
 & \times \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}} \right) = (-1)^{f(0)} \left(\frac{|0\rangle + (-1)^{f(0) \oplus f(1)}|1\rangle}{\sqrt{2}} \right) \\
 & \quad \times \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}} \right),
 \end{aligned}$$



NMR pulse sequence

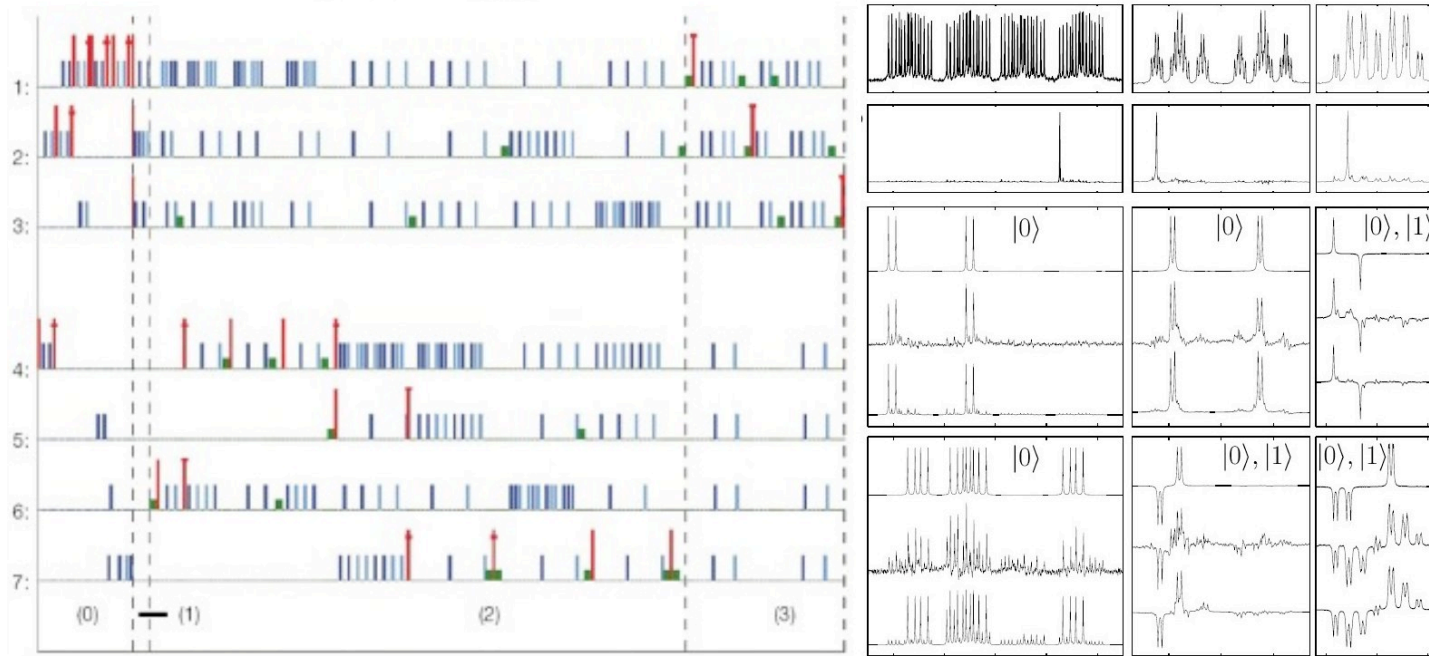
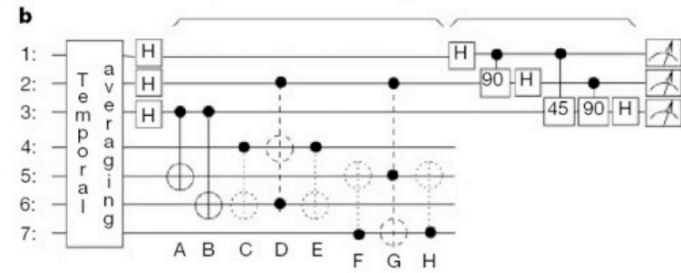
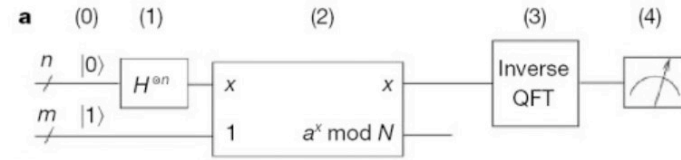
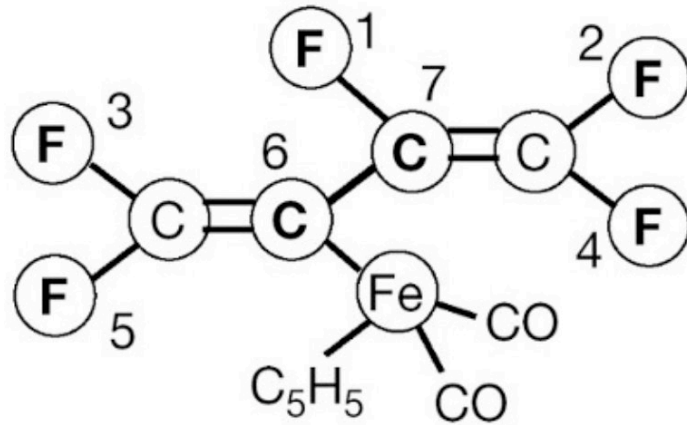


NMR results



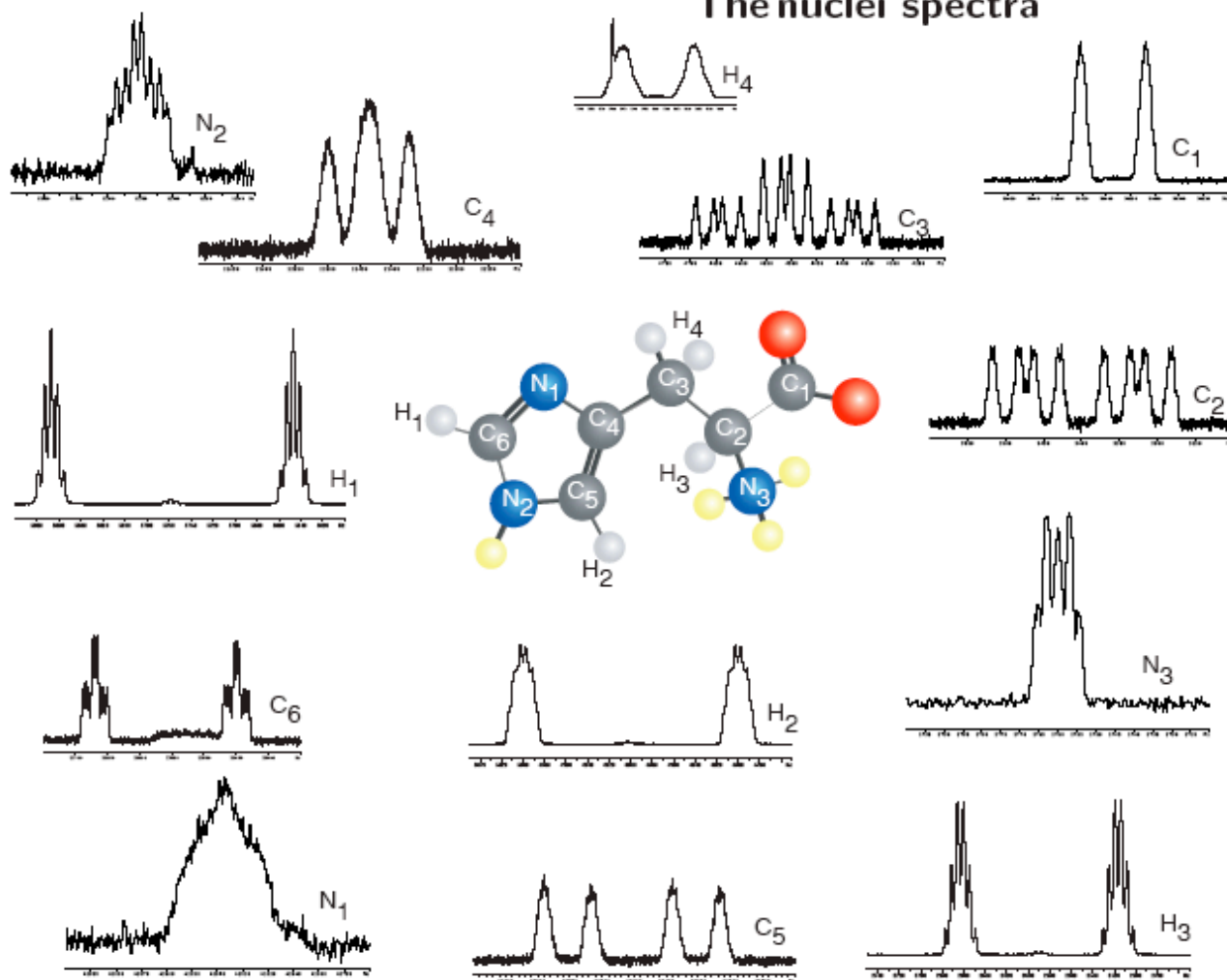
Jones and Mosca, 1998

Factoring 15...Vandersypen et al, 2001



Current experiments at IQC: 12-qubit NMR QIP

The nuclei spectra



Relaxation and decoherence

General Kraus operator sum:

$$\rho \rightarrow \sum_k A_k \rho A_k^\dagger \quad \sum_k A_k^\dagger A_k = I$$

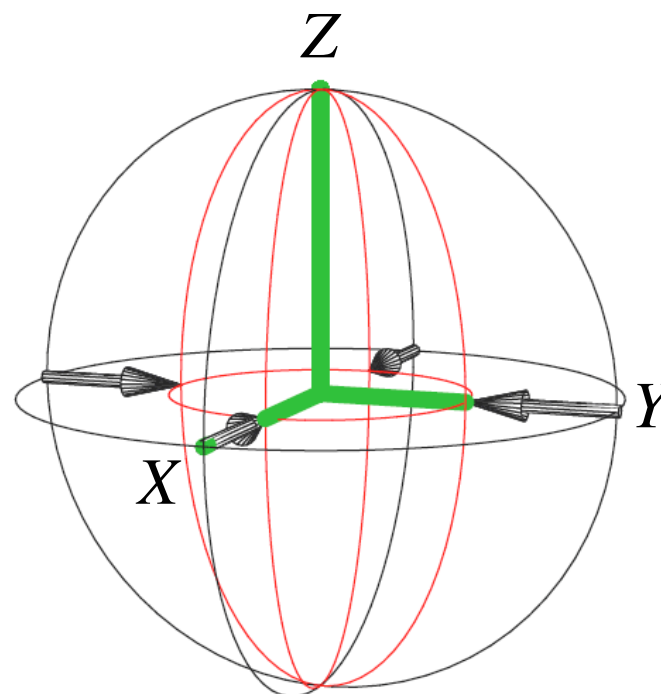
	Spin operators
Relaxation	σ_x, σ_y
Dephasing	σ_z

Example: pure dephasing

$$A = e^{-i\phi\sigma_z}$$

$$\rho \rightarrow \int d\phi \left(e^{-i\phi\sigma_z} \rho e^{i\phi\sigma_z} f(\phi, t, T_2) \right) \rightarrow \begin{pmatrix} a & be^{-t/T_2} \\ b^* e^{-t/T_2} & 1-a \end{pmatrix}$$

Lorentzian with
time-dependent
FWHM



Dephasing on the Bloch sphere

Pure dephasing

Or in another form:

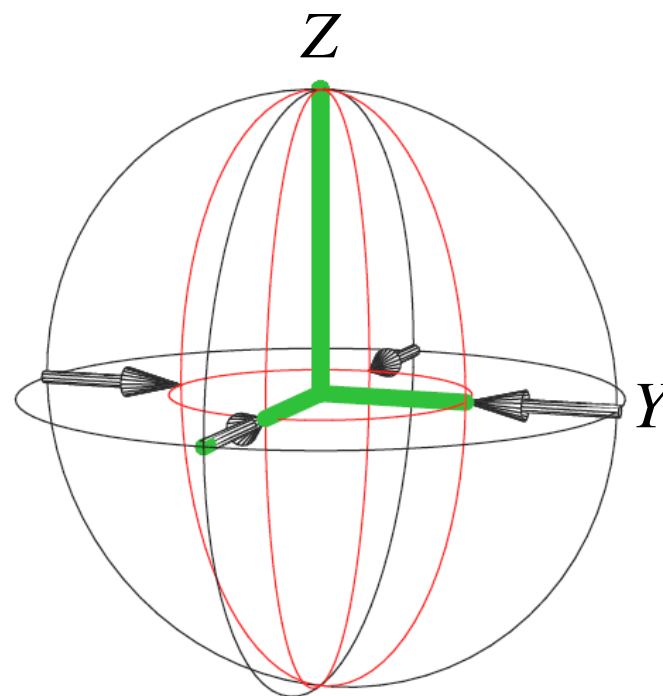
$$\Lambda(\rho) = (1-p)|\psi\rangle\langle\psi| + p\sigma_z|\psi\rangle\langle\psi|\sigma_z$$

With Kraus operators:

$$A_0 = \sqrt{1-p}\mathbf{I}$$

$$A_1 = \sqrt{p}\sigma_z$$

$$p = \frac{1 - e^{-t/T_2}}{2}$$



Dephasing on the Bloch sphere

Relaxation

$$A_0 = \sqrt{p} \begin{pmatrix} 1 & 0 \\ 0 & \sqrt{1-\eta} \end{pmatrix} \quad A_2 = \sqrt{1-p} \begin{pmatrix} \sqrt{1-\eta} & 0 \\ 0 & 1 \end{pmatrix}$$

$$A_1 = \sqrt{p} \begin{pmatrix} 0 & \sqrt{\eta} \\ 0 & 0 \end{pmatrix} \quad A_3 = \sqrt{1-p} \begin{pmatrix} 0 & 0 \\ \sqrt{\eta} & 0 \end{pmatrix}$$

see e.g. Nielsen & Chuang

$$\Lambda(\rho) = \begin{pmatrix} (a - a_0)e^{-t/T_1} + a_0 & be^{-t/2T_1} \\ b^*e^{-t/2T_1} & (a_0 - a)e^{-t/T_1} + (1 - a_0) \end{pmatrix}$$

For pure relaxation, $T_2 = 2T_1$

In liq. state NMR, typically

$$T_2 \sim 0.5-5 \text{ s}$$

$$T_1 \sim 5-20 \text{ s}$$