NmR with a small ‘m’:
Low Field Magnetic Resonance

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S S E

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Current state of the art in High Field Magnetic Resonance

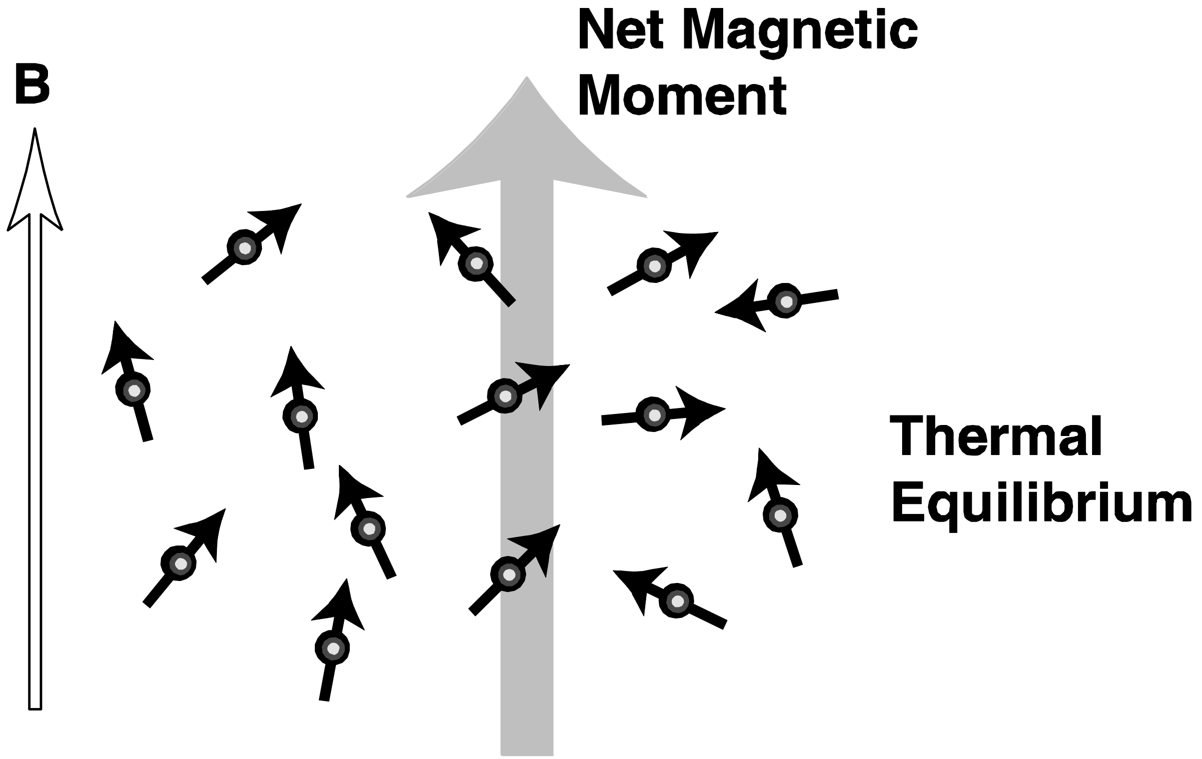
Cryogens
Bulky and immobile
Expensive
Maintenance
Specialist Training


VARIAN

Quantum Description of NMR

Zeeman interaction

$$H_o = -\gamma \hat{I} \bullet B_o = \omega_o I_z$$



States in an NMR experiment

$$\rho = \sum_k w_k \left|\psi_k\right\rangle\left\langle\psi_k\right|; \sum_k w_k = 1$$

$$\rho_{eq} = \frac{\exp\left(-H_o / k_B T\right)}{Tr\left[\exp\left(-H_o / k_B T\right)\right]}$$

Liouville-von Neumann Equation

$$\rho(t) = \exp\left(-i\left(H_{\text{int}} + H_{ext}\right)(t - t_0)\right)\rho(t_0)\exp\left(i\left(H_{\text{int}} + H_{ext}\right)(t - t_0)\right)$$

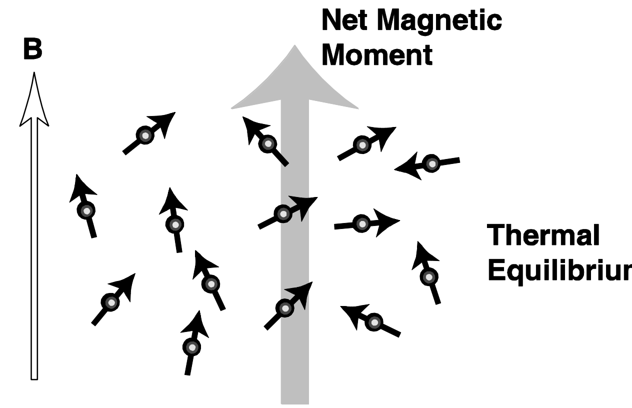
Equilibrium state

$$\rho_{eq} = \frac{\exp\left(-H_o / k_B T\right)}{Tr\left[\exp\left(-H_o / k_B T\right)\right]} = \frac{\exp\left(-\omega_o \hat{I}_z / k_B T\right)}{Tr\left[\exp\left(-\omega_o \hat{I}_z / k_B T\right)\right]}$$

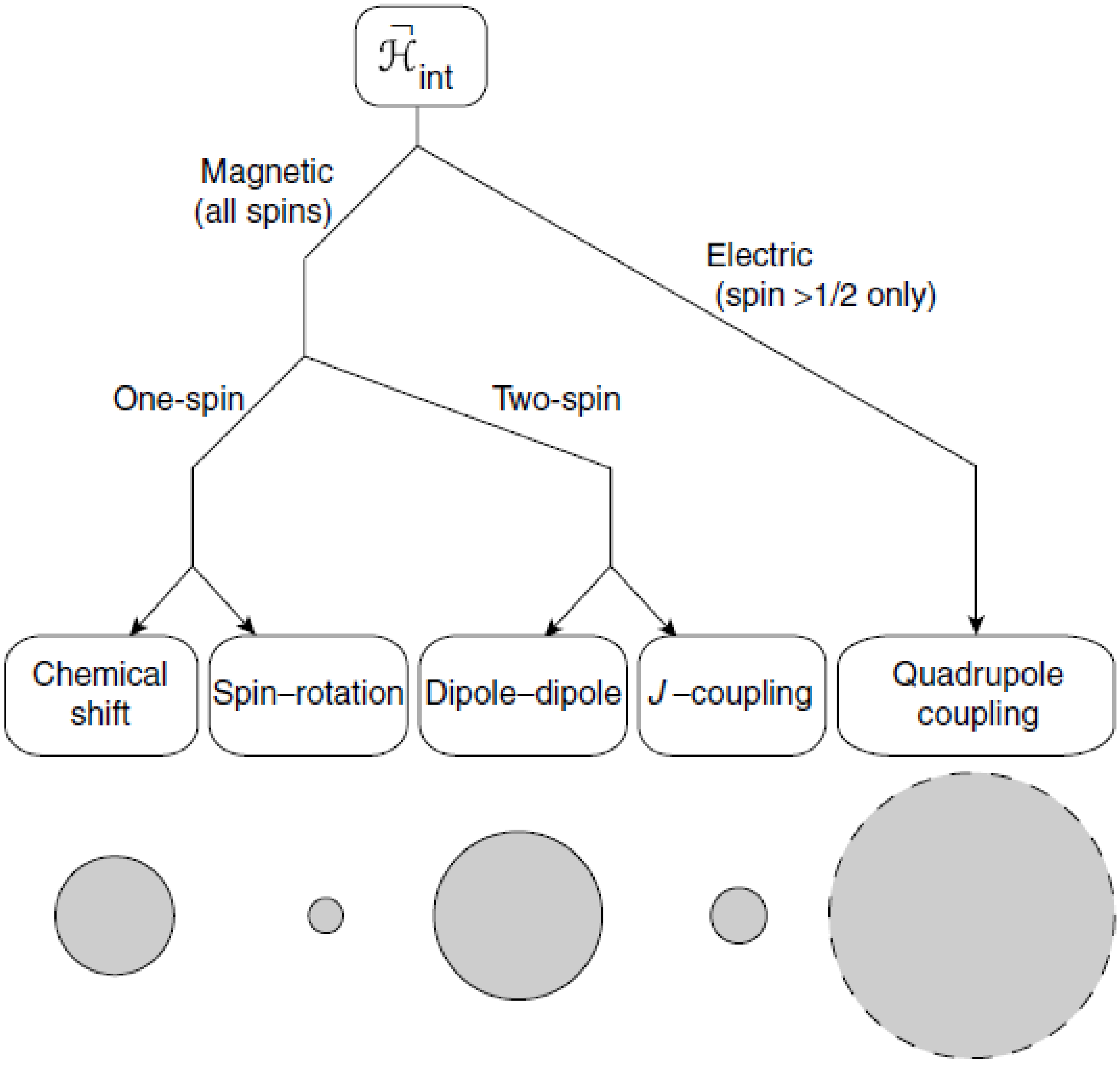
$$\rho_{eq} = \frac{1}{2\cosh\left(\hbar\omega_o / 2k_B T\right)} \mathrm{diag}\left\{\exp\left(-\hbar\omega_o / 2k_B T\right), \exp\left(+\hbar\omega_o / 2k_B T\right)\right\}$$

$$= \frac{1}{2}\mathrm{diag}\left\{1 - \hbar\omega_o / 2k_B T, 1 + \hbar\omega_o / 2k_B T\right\} = \frac{1}{2} + \varepsilon I_z$$

$$\varepsilon = \hbar\omega_o / 2k_B T \approx 10^{-5}$$



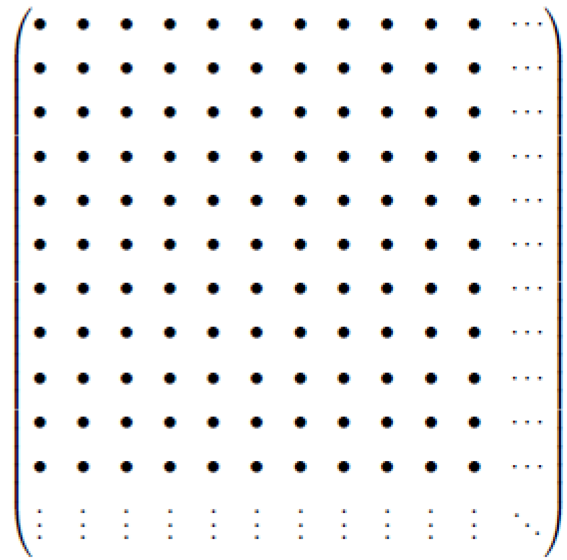
Nuclear Spin Hamiltonian



Two Important Simplifications

Secular Approximation

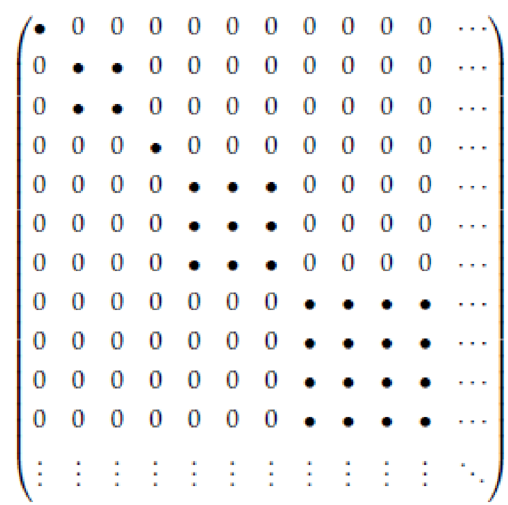
$$H = A + B; \quad \|A\| > \|B\|$$



$$A|n\rangle = a_n |n\rangle$$

$$[A, B] \neq 0$$

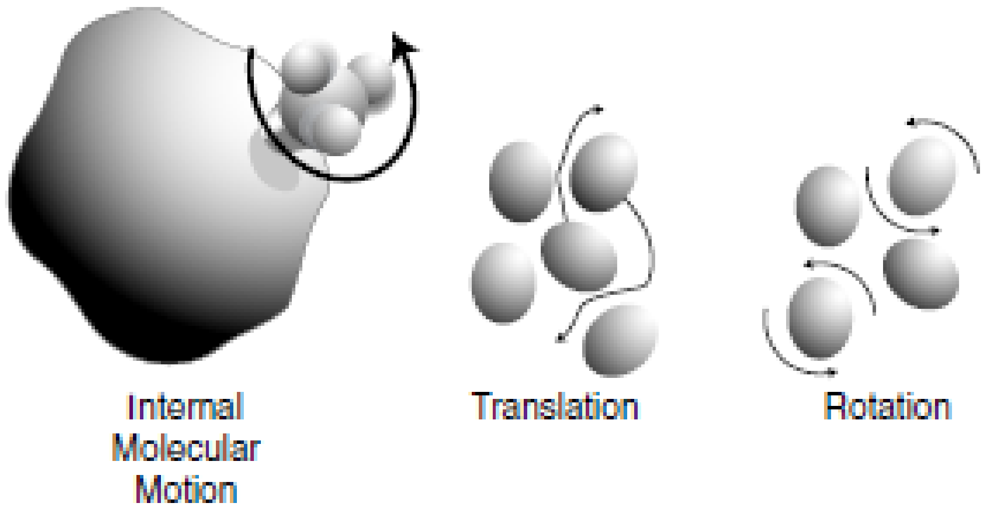
$$B_o = \sum_n b_{nn} |n\rangle\langle n| + \sum_{n \neq m}' b_{nm} |n\rangle\langle m|$$



$$|b_{nm}| < |a_n - a_m|$$

$$[B_o, A] \neq 0$$

Motional Averaging

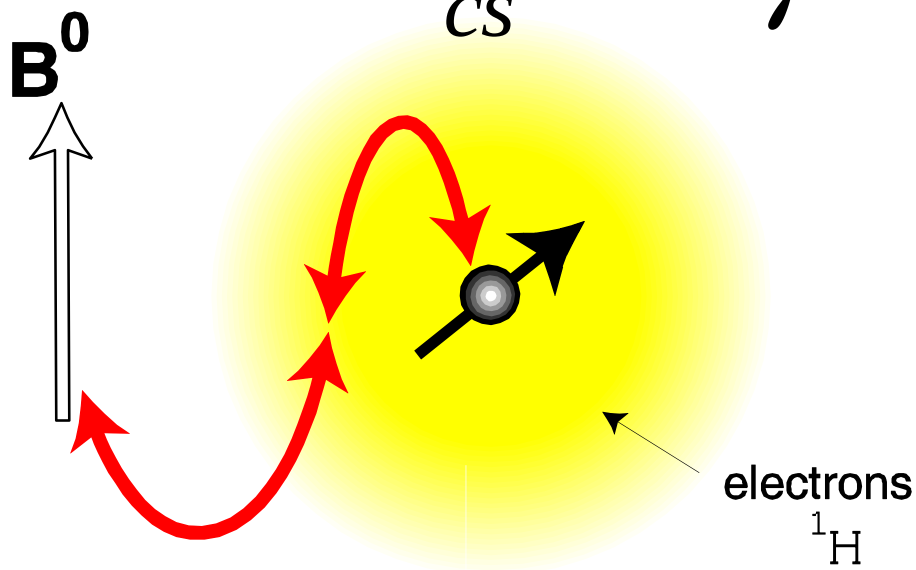


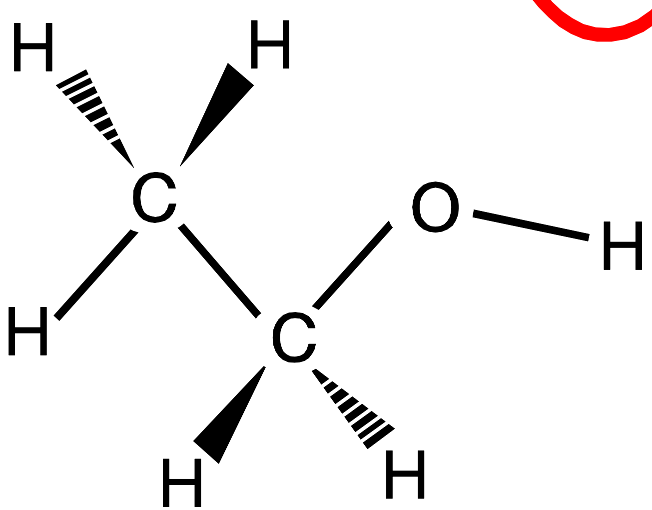
$$\langle H \rangle_t = \bar{H} = \frac{1}{N} \int_{\Theta} d\Theta\, p(\Theta) H(\Theta)$$

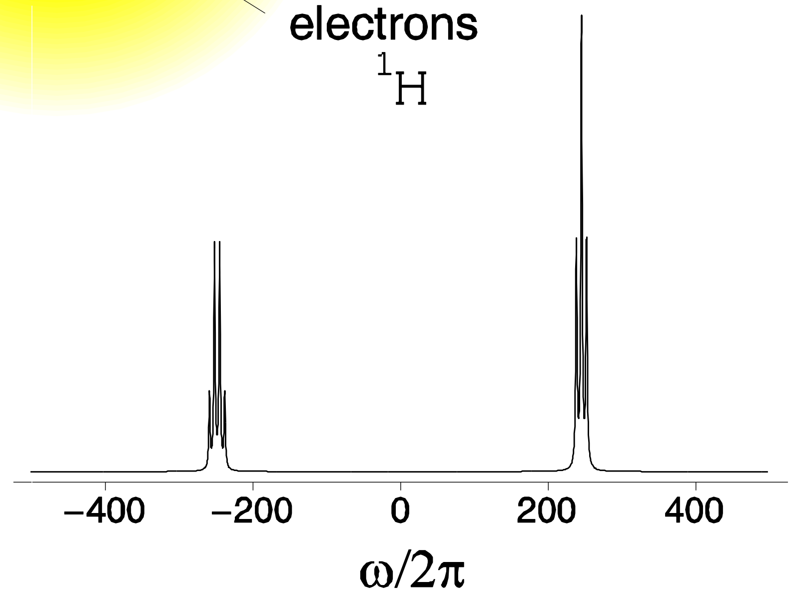
$$N = \int_{\Theta} d\Theta\, p(\Theta)$$

Chemical Shift interaction

$$H_{cs} = -\gamma I \bullet \hat{\hat{\delta}} \bullet B_o$$







Applying the approximations to CS interaction

$$H_{cs} = -\gamma(I_x, I_y, I_z)\begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ B_o \end{pmatrix}$$

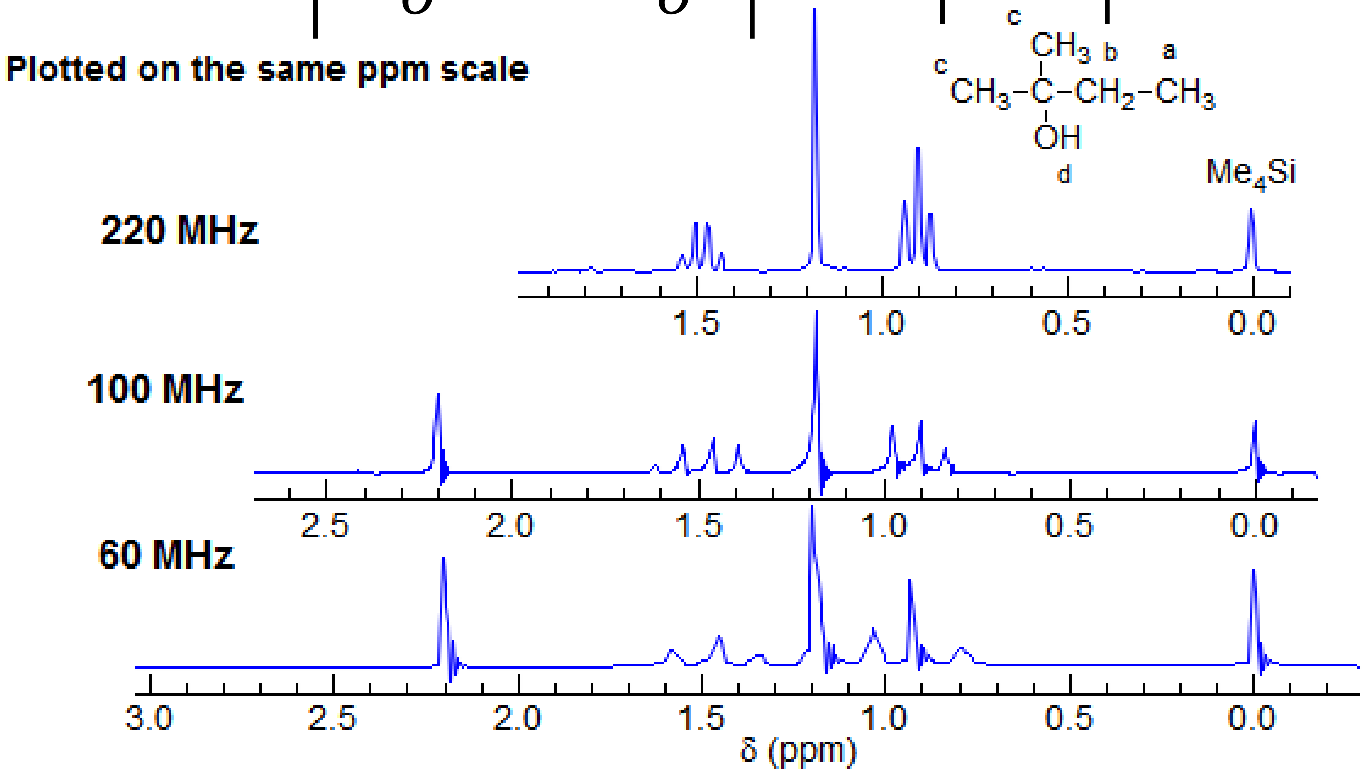
$$= -\gamma(\delta_{xz} I_x + \delta_{yz} I_y + \delta_{zz} I_z)B_o \approx -\gamma\delta_{zz}(\Theta)B_o I_z$$

$$\delta(\alpha,\beta,\gamma) = R(\alpha,\beta,\gamma)\delta(0,0,0)R^{-1}(\alpha,\beta,\gamma)$$

$$R(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & -\sin\alpha\cos\gamma - \cos\alpha\cos\beta\sin\gamma & \cos\alpha\sin\beta \\ \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\alpha\sin\beta \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{pmatrix}$$

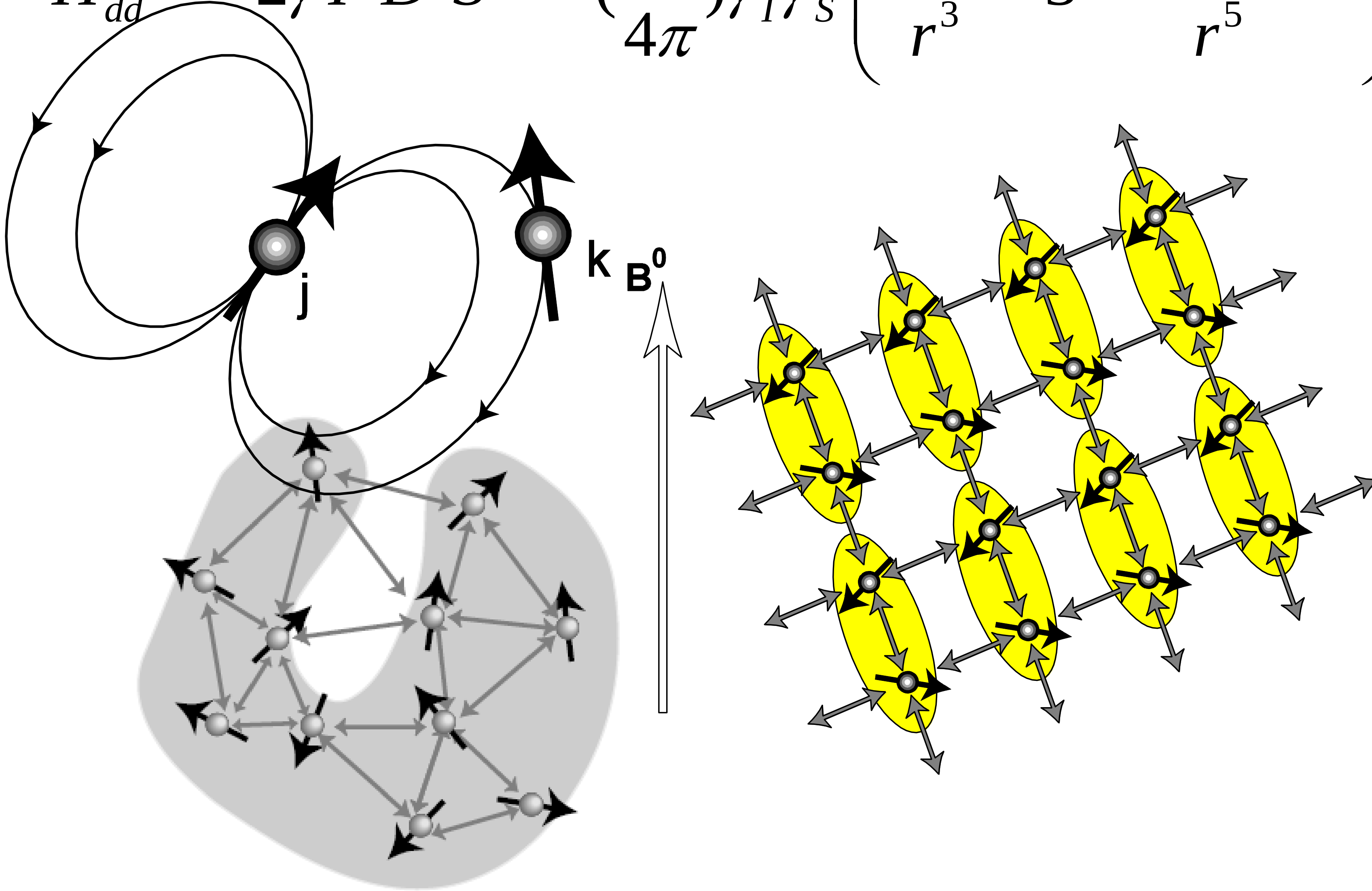
$$\overline{\delta(\alpha,\beta,\gamma)}_{zz} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz}) = \frac{1}{3}Tr(\delta) = \delta^{iso}$$

$$\left|\omega_o{}^j - \omega_o{}^k\right| >> \left|\pi J\right|$$



Dipolar interaction

$$H_{dd} = -2\gamma \hat{I}\bullet\hat{\hat{D}}\bullet S = -(\frac{\mu_o}{4\pi})\gamma_I \gamma_S \left(\frac{\hat{I}\bullet S}{r^3} - 3\frac{(\hat{I}\bullet\vec{r})(S\bullet\vec{r})}{r^5} \right)$$



Homonulear spins

$$H_{dd}^{jk}(\Theta_{jk}) = d_{jk}(3I_{jz}I_{kz} - I_j \bullet I_k)$$

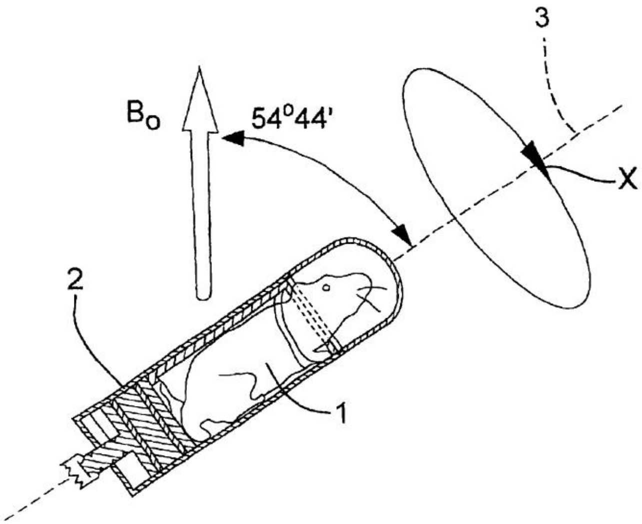
$$d_{jk} = -(\frac{\mu_o}{4\pi})\gamma_I\gamma_S\frac{1}{2}(3\cos^2\theta_{jk} - 1)$$

Heteronulear spins

$$H_{dd}^{jk}(\Theta_{jk}) = d_{jk}(2I_{jz}I_{kz})$$

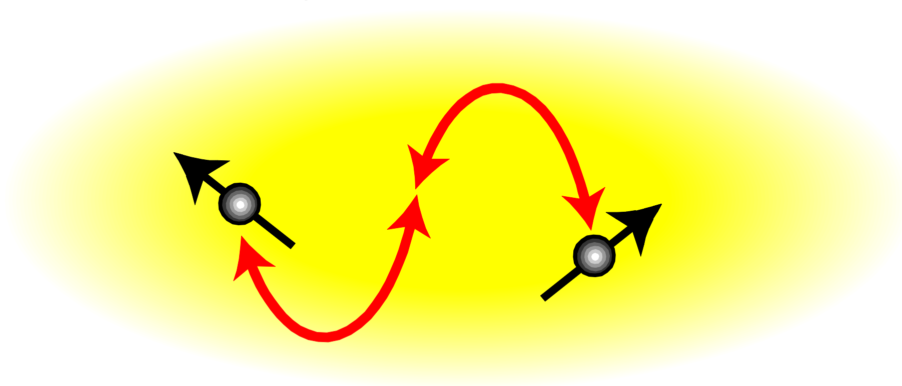
$$\int_0^{\pi}\sin\theta_{jk}(3\cos^2\theta_{jk} - 1)d\theta = 0$$

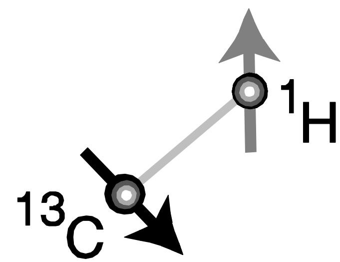
$$\bar{H}_{dd} = 0$$

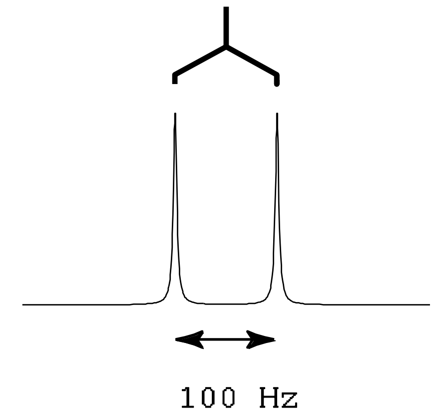


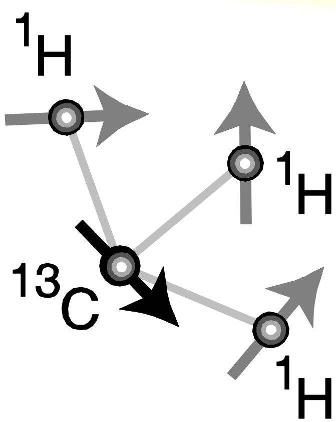
Scalar(J) interaction

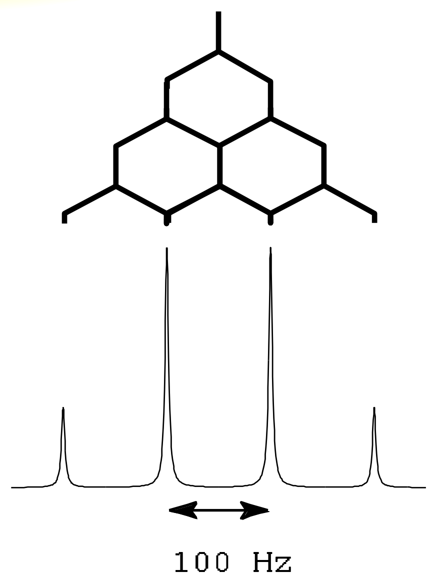
$$H_J = 2\pi \hat{I} \bullet \hat{\hat{J}} \bullet S$$

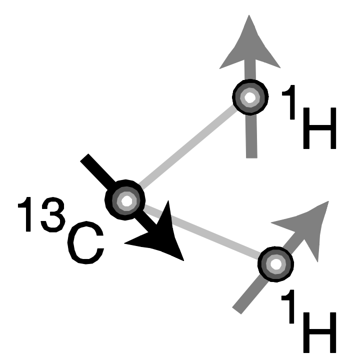


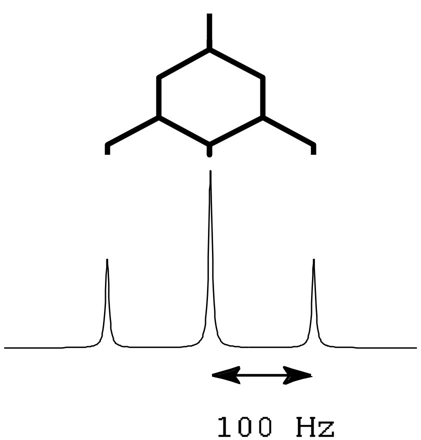












Homonulear spins

$$H_J^{jk} = 2\pi J^{iso}(I_j \bullet I_k)$$

Heteronulear spins $|\omega_o^j - \omega_o^k| >> |\pi J|$

$$H_J^{jk} = \pi J^{iso}(2I_{jz}I_{kz})$$

Approximate internal Hamiltonian

$$H = H_{cs} + H_J$$

$$= \omega_o(1-\sigma_{cs})I_z + \pi J^{iso}(2I_{jz}I_{kz})$$ heteronuclear

$$\omega_o(1-\sigma_{cs})I_z + 2\pi J^{iso}(I_j \bullet I_k)$$ homonuclear

Quadrupolar interaction

$$H_Q = \frac{eQ}{2I(2I-1)} \hat{I} \bullet V \bullet \hat{I}$$

$$H_{\text{int}} = H_{dd} + H_{cs} + H_J + H_Q$$

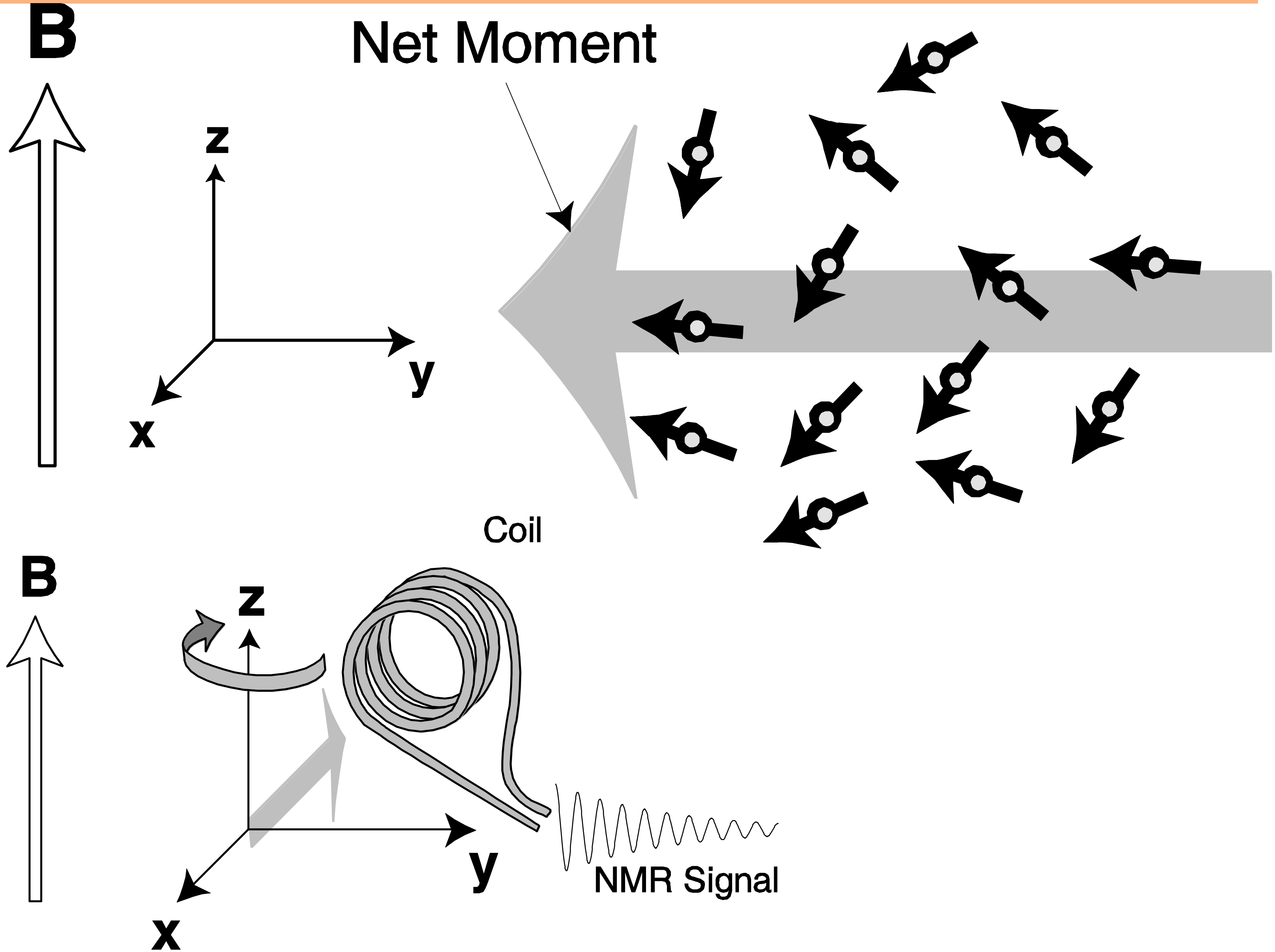
$$H_{ext} = H_0 + H_{rf}$$

Radiofrequency interaction

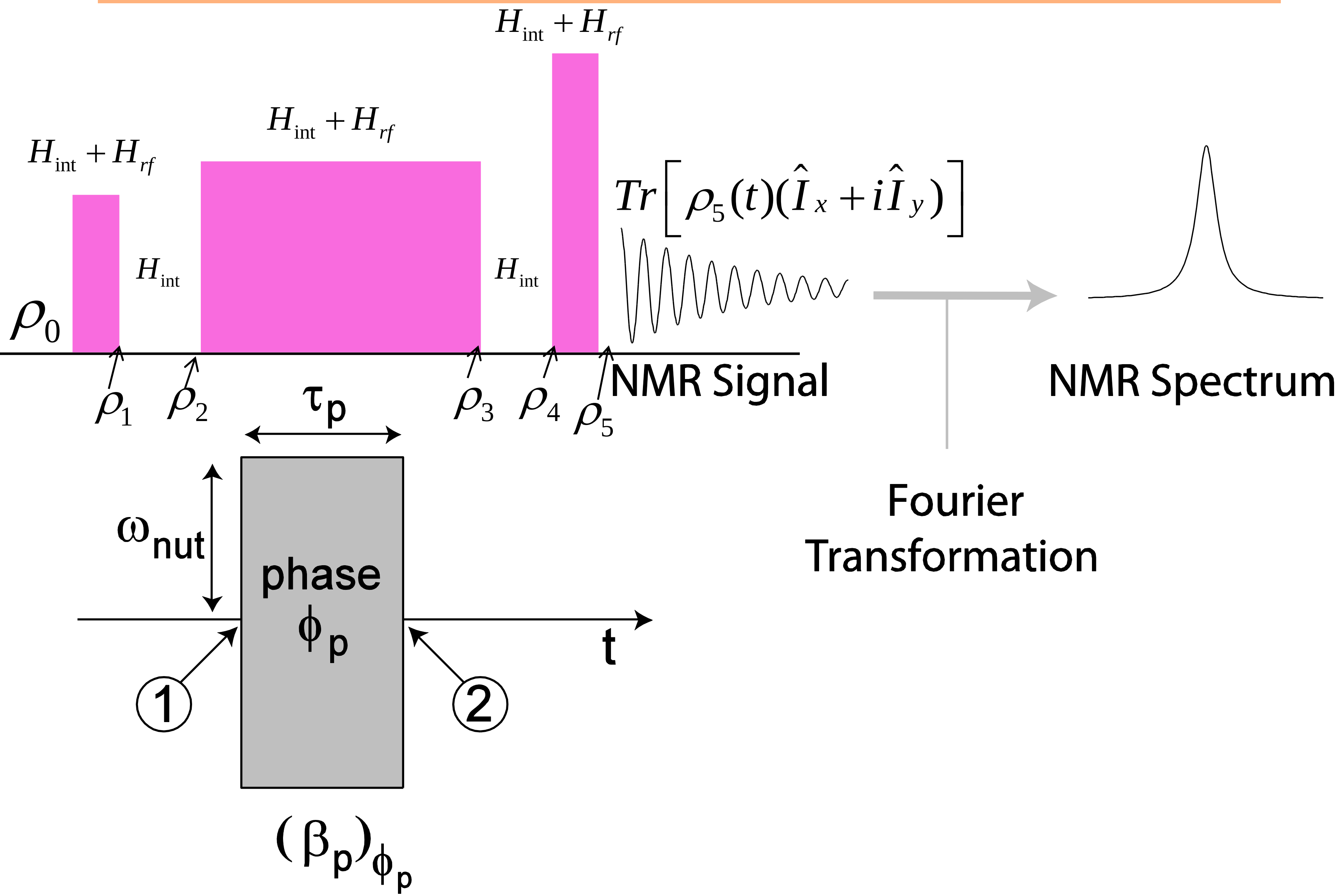
$$H_{rf} = -\gamma \frac{B_1}{2} \left(\cos\left(\omega_{tr} t + \phi\right) \hat{I}_x + \sin\left(\omega_{tr} t + \phi\right) \hat{I}_y \right)$$

$$= \frac{\omega_1}{2} \left(\cos\left(\omega_{tr} t + \phi\right) \hat{I}_x + \sin\left(\omega_{tr} t + \phi\right) \hat{I}_y \right)$$

Role of an NMR pulse

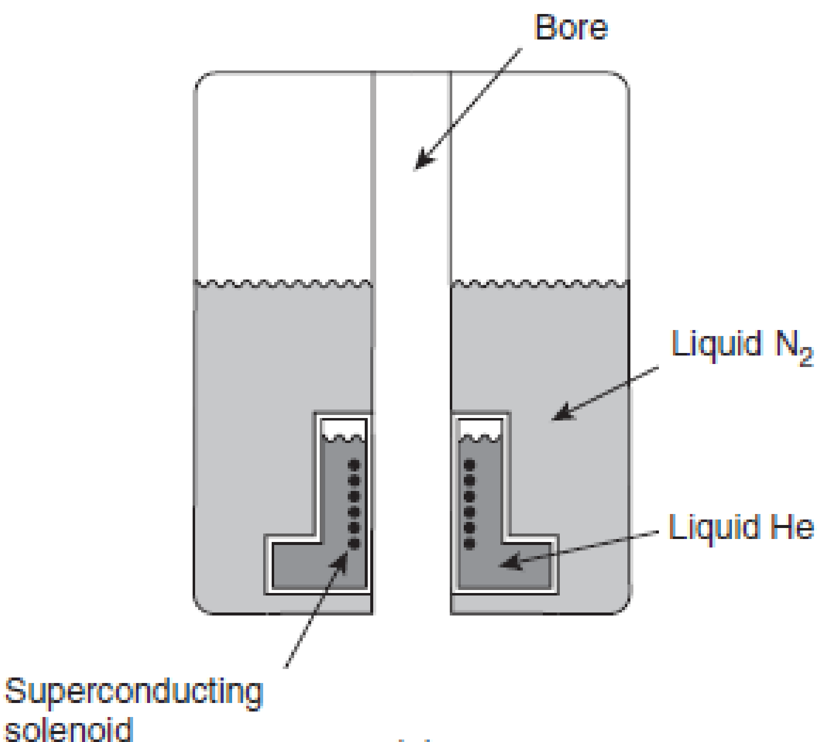


Scheme of an NMR experiment

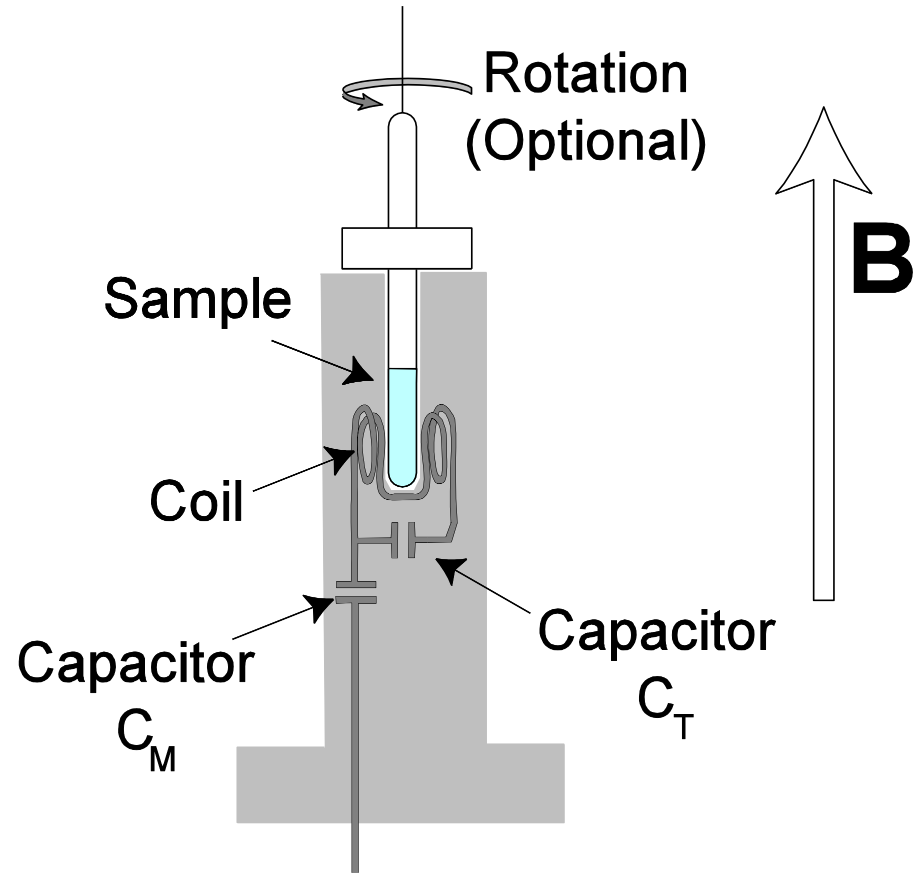


High field instrumentation

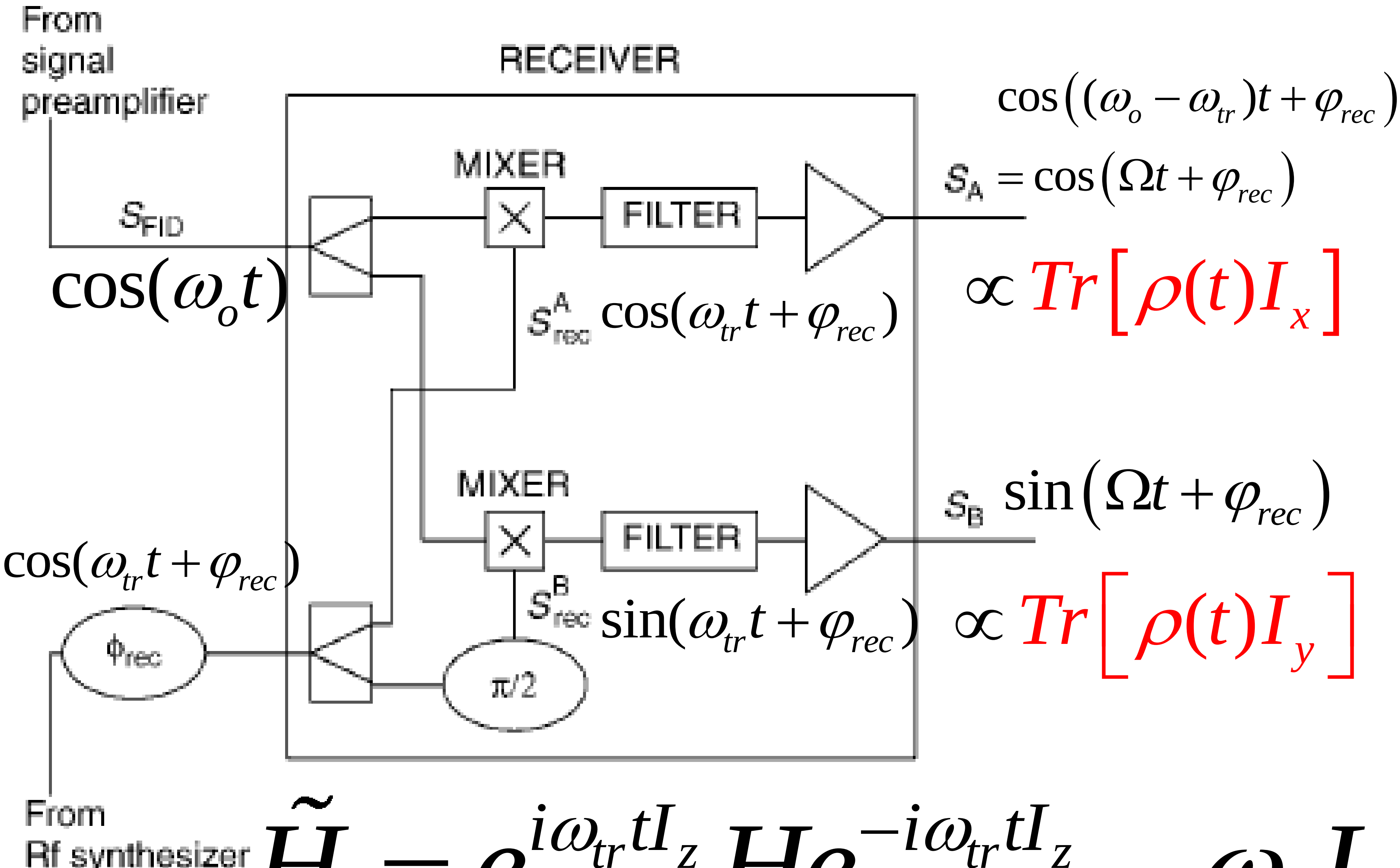
Overview of the system



(a)



Signal detection in the high field



$$\tilde{H} = e^{i\omega_{tr} t I_z} H e^{-i\omega_{tr} t I_z} - \omega_o I_z$$

$$s(t) \propto Tr\left[\rho(t) I_x\right] - iTr\left[\rho(t) I_y\right] = Tr\left[\rho(t) I^-\right]$$

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \boxed{\rho_{21}} & \rho_{22} \end{pmatrix} = \begin{pmatrix} \rho_\alpha & \rho_+ \\ \boxed{\rho_-} & \rho_\beta \end{pmatrix} = \rho_\alpha I^\alpha + \rho_\beta I^\beta + \rho_+ I^+ + \rho_- I^-$$

$$\hat{\rho} = \begin{pmatrix} \rho_{\boxed{\alpha\alpha}} & \rho_{\boxed{\alpha+}} & \rho_{\boxed{+\alpha}} & \rho_{\boxed{++}} \\ \rho_{\boxed{\alpha-}} & \rho_{\boxed{\alpha\beta}} & \rho_{\boxed{+-}} & \rho_{\boxed{+\beta}} \\ \rho_{\boxed{-\alpha}} & \rho_{\boxed{-+}} & \rho_{\boxed{\beta\alpha}} & \rho_{\boxed{\beta+}} \\ \rho_{\boxed{--}} & \rho_{\boxed{-\beta}} & \rho_{\boxed{\beta-}} & \rho_{\boxed{\beta\beta}} \end{pmatrix}$$

Strong coupling calculations (going to low fields)

$$H = \Omega_1^o I_{1z} + \Omega_2^o I_{2z} + 2\pi J I_1 \bullet I_2$$

$$= \frac{1}{2}\begin{pmatrix} \Omega_1 + \Omega_2 + \pi J & 0 & 0 & 0 \\ 0 & \Omega_1 - \Omega_2 - \pi J & 2\pi J & 0 \\ 0 & 2\pi J & -\Omega_1 + \Omega_2 - \pi J & 0 \\ 0 & 0 & 0 & -\Omega_1 - \Omega_2 + \pi J \end{pmatrix}$$

$$|1\rangle = |\alpha\alpha\rangle; \qquad |4\rangle = |\beta\beta\rangle$$

$$|2\rangle = \cos\frac{\xi}{2}|\alpha\beta\rangle + \sin\frac{\xi}{2}|\beta\alpha\rangle$$

$$|3\rangle = -\sin\frac{\xi}{2}|\alpha\beta\rangle + \cos\frac{\xi}{2}|\beta\alpha\rangle$$

$$\tan\frac{\xi}{2} = \frac{2\pi J}{\Omega_1^o - \Omega_2^o}$$

$$\Omega_1 = \frac{1}{2}\left(\Omega_1^o + \Omega_2^o + \pi J\right)$$

$$\Omega_4 = \frac{1}{2}\left(-\Omega_1^o - \Omega_2^o + \pi J\right)$$

$$\Omega_2 = -\frac{\pi J}{2} + \frac{1}{2}\sqrt{(2\pi J)^2 + (\Omega_1^o - \Omega_2^o)^2}$$

$$\Omega_3 = -\frac{\pi J}{2} - \frac{1}{2}\sqrt{(2\pi J)^2 + (\Omega_1^o - \Omega_2^o)^2}$$

$$\hat{\rho} = \begin{pmatrix} \rho_{\boxed{\alpha\alpha}} & \rho_{\boxed{\alpha+}} & \rho_{\boxed{+\alpha}} & \rho_{\boxed{++}} \\ \rho_{\boxed{\alpha-}} & \rho_{\boxed{\alpha\beta}} & \rho_{\boxed{+-}} & \rho_{\boxed{+\beta}} \\ \rho_{\boxed{-\alpha}} & \rho_{\boxed{-+}} & \rho_{\boxed{\beta\alpha}} & \rho_{\boxed{\beta+}} \\ \rho_{\boxed{--}} & \rho_{\boxed{-\beta}} & \rho_{\boxed{\beta-}} & \rho_{\boxed{\beta\beta}} \end{pmatrix}$$

$$I_{1z} + I_{2z} \xrightarrow{\text{pulse}} -I_{1y} - I_{2y}$$

$$\rho_{rs}(0) = -\left\langle r \middle| (I_{1y} + I_{2y}) \middle| s \right\rangle$$

$$\rho_{21}(0) = \rho_{42}(0) = \frac{1}{2i}\left(\cos\frac{\xi}{2} + \sin\frac{\xi}{2}\right)$$

$$\rho_{31}(0) = \rho_{43}(0) = \frac{1}{2i}\left(\cos\frac{\xi}{2} - \sin\frac{\xi}{2}\right)$$

$$\rho_{rs}(t) = \rho_{rs}(0)\exp\left(-i(\Omega_r - \Omega_s)t\right)e^{-\lambda t}$$

$$\left\langle I^- \right\rangle(t) = \sum_r \sum_s \rho_{rs}(t) \left\langle r \middle| I^- \middle| s \right\rangle$$

$$\propto a_{21}\exp\left(-i(\Omega_2 - \Omega_1)t\right) + a_{31}\exp\left(-i(\Omega_3 - \Omega_1)t\right)$$

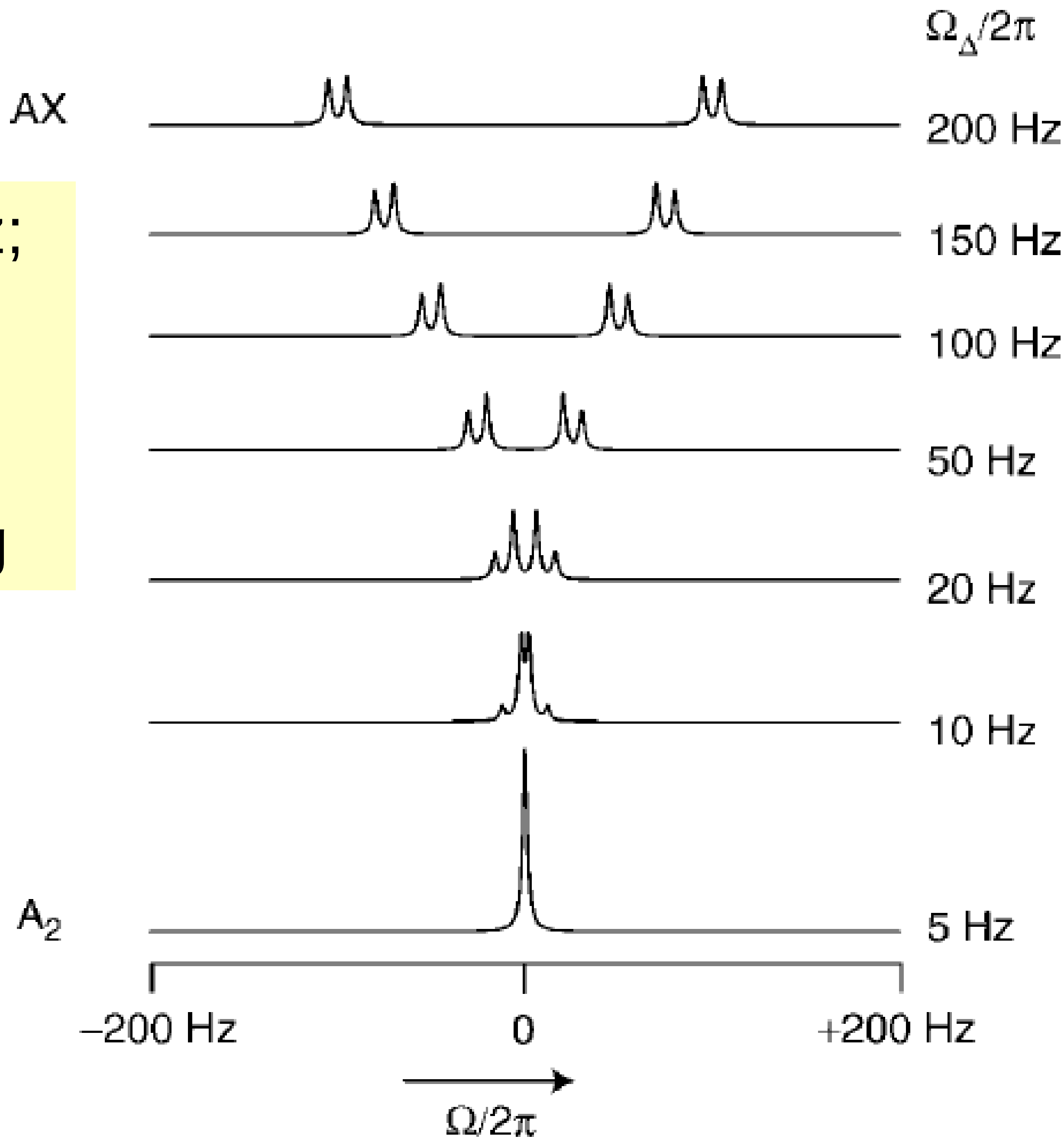
$$+a_{42}\exp\left(-i(\Omega_4 - \Omega_2)t\right) + a_{43}\exp\left(-i(\Omega_4 - \Omega_3)t\right)$$

$$a_{21} = a_{42} = \frac{1}{2}(1 + \sin\xi)$$

$$a_{31} = a_{43} = \frac{1}{2}(1 - \sin\xi)$$

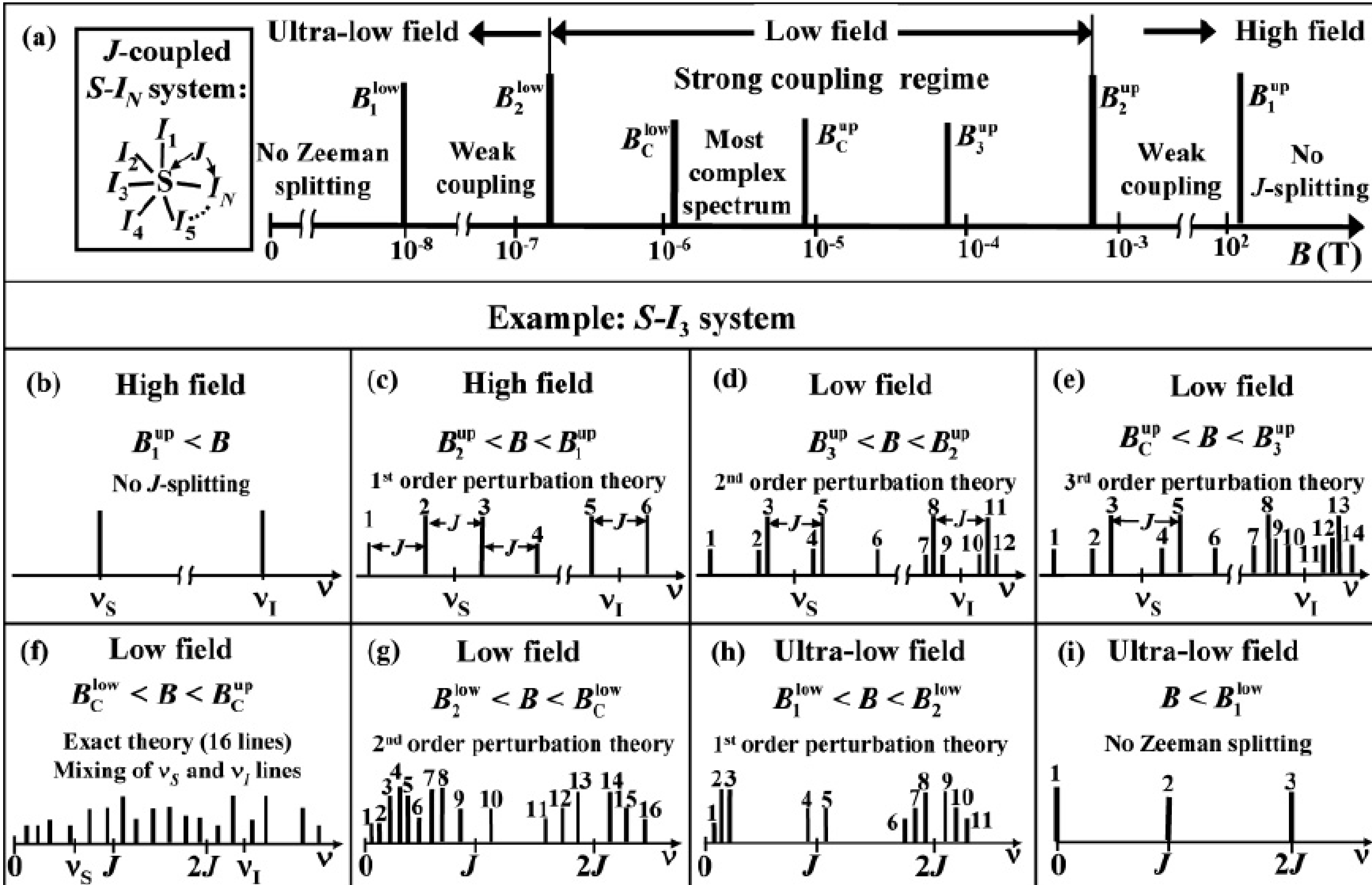
J=10 Hz;

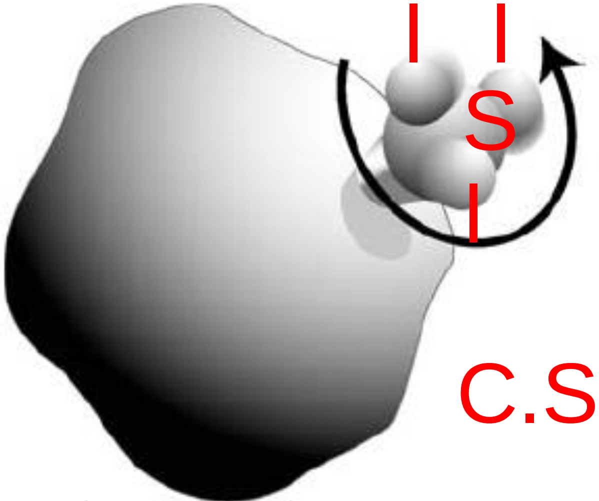
Zero dipole coupling



Calculating spectra for arbitrary spin topologies

S. Appelt *et al.* PRA 81, 023420 (2010)





$$H = \omega_S S_z + \omega_I \underbrace{\sum_{k=1}^{N} I_{kz}}_{H^z} + \underbrace{2\pi J \vec{S} \cdot \sum_{k=1}^{N} \vec{I}_k}_{H^{\text{het}}},$$

C.S.C.O. at high fields

$S^2, S_z, F_I^{\,2}, F_z$

$s = 1/2, m_s = 1/2, -1/2, F_I = N/2 - k$ where $k = 0, 1, \ldots, N/2\text{-}1/2$

$$E(F_I, m_I, m_S) = (m_I + m_S)\nu_I - \frac{J}{4} + m_S \times \sqrt{(F_I + 1/2)^2 J^2 + 2J(m_I + m_S)(\nu_S - \nu_I) + (\nu_S - \nu_I)^2}.$$

$$E(F_I, m_I, m_S) = m_I \nu_I + m_S \nu_S + \left[m_S(m_I + m_S) - \frac{1}{4}\right] J + \frac{m_S}{2}[(F_I + 1/2)^2 - (m_I + m_S)^2] \frac{J^2}{\nu_S - \nu_I}$$

C.S.C.O. at low fields

$$F^2, F_z$$

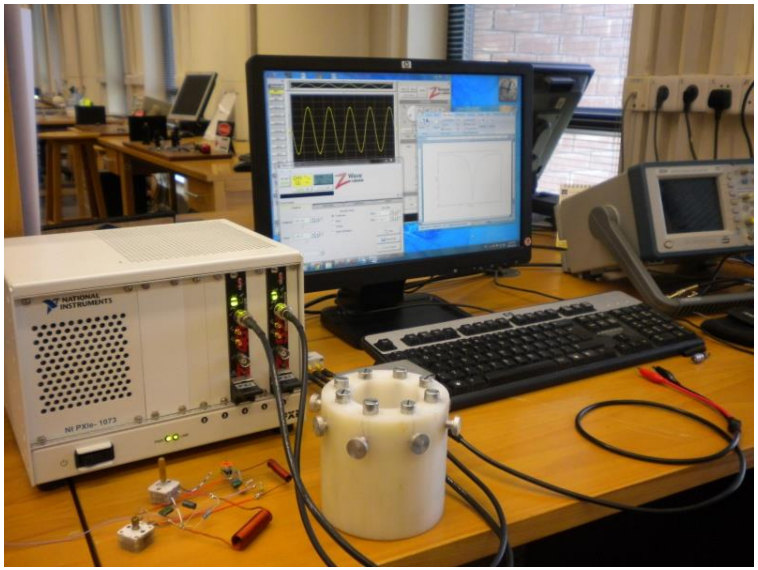
$$F, m_F \text{ where } F = F_I + S$$

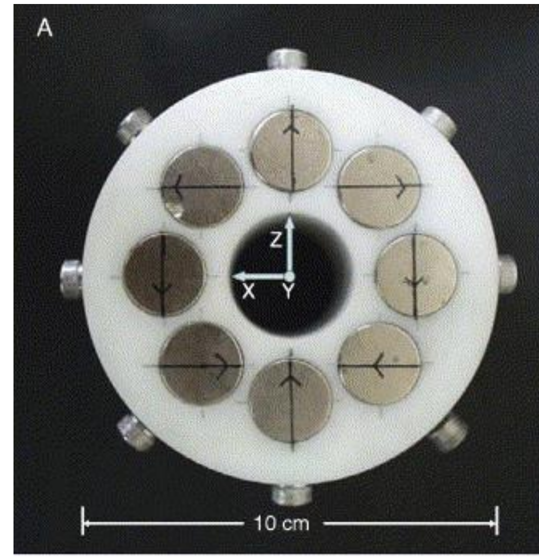
$$E(F_I, F_S, m_F) = m_F \nu_I - \frac{J}{4} + F_S \times \sqrt{(F_I + 1/2)^2 J^2 + 2 m_F J (\nu_S - \nu_I) + (\nu_S - \nu_I)^2}.$$

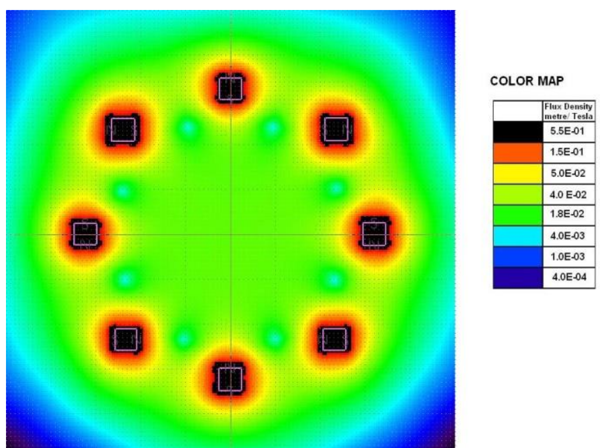
$$E(F_I, F_S, m_F) = \left[F_S (F_I + 1/2) - \frac{1}{4}\right] J + \left[1 - \frac{F_S}{F_I + 1/2}\right] m_F \nu_I + \left[\frac{F_S}{F_I + 1/2}\right] m_F \nu_S + F_S \frac{(F_I + 1/2)^2 - m_F^2}{2 (F_I + 1/2)^3} \frac{(\nu_S - \nu_I)^2}{J}$$

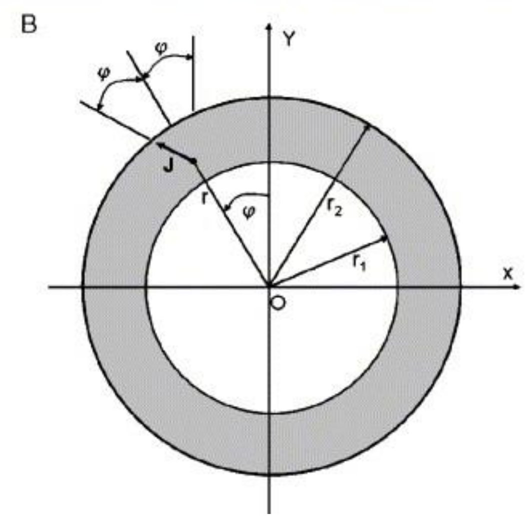
Miniaturizing NMR

Compact permanent magnets

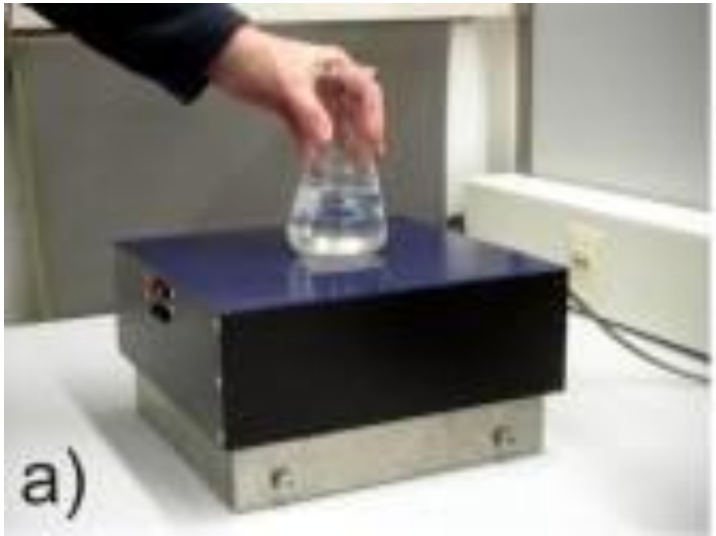


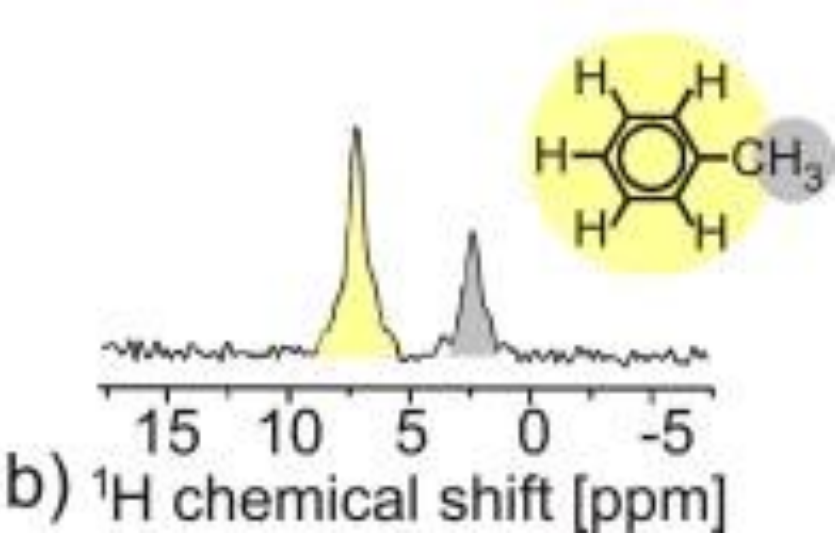






NMR in stray fields

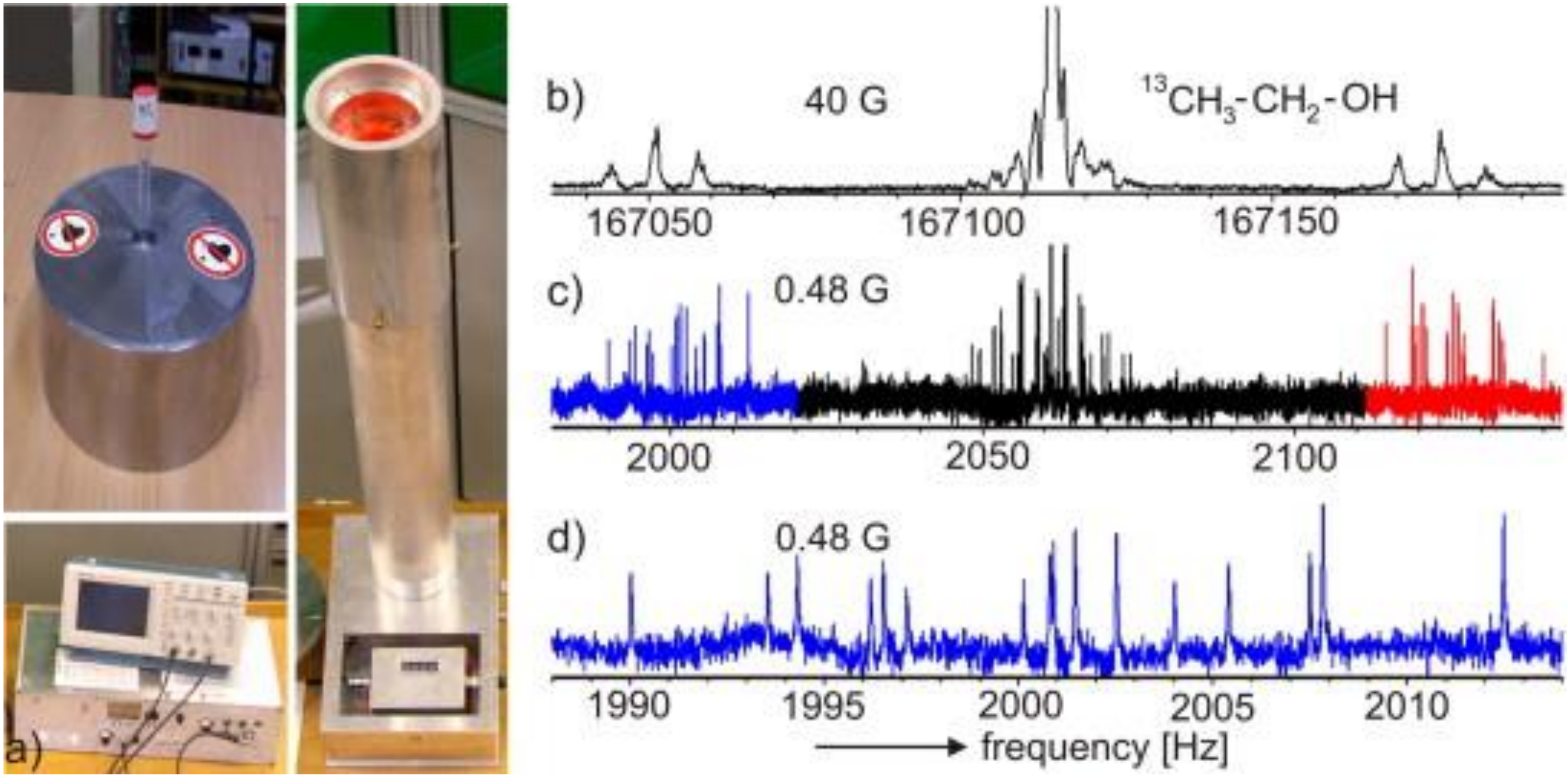




Bluemich *et al*., Chem. Phys. Lett. 477, 231-240 (2009).

One-sided electromagnets

NMR in the earth's field



S. Appelt *et al.*, Nature Phys. 2, 105 (2006).

Role of the external magnetic field

Sensitivity

$$\xi = \kappa\left(\frac{B_r}{i_r}\right)V_s\omega_0 M = \kappa\left(\frac{B_r}{i_r}\right)V_s\omega_0 P N_s \mu$$

$$\omega_0 \propto B; P \propto B$$

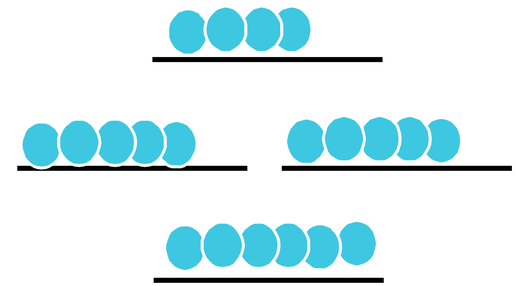
$$\xi \propto \kappa V_s B^2 N_s$$

$$\rho_{i,eq} = \exp\left(-E_i / k_B T\right) / Z$$

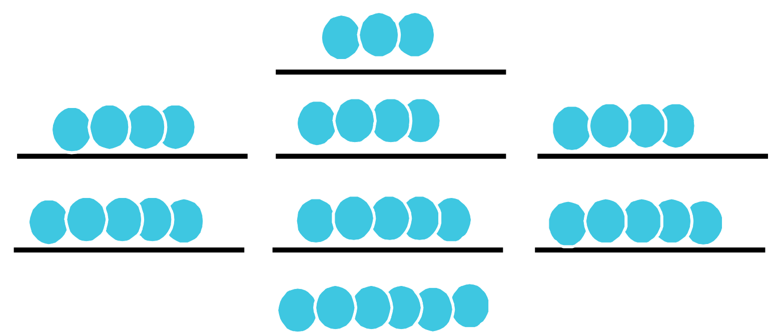
$$\Delta E = \gamma\hbar B = \hbar\omega_0 = 2.8\times10^{-25}\ J$$

$$k_B T = 4\times10^{-21}\ J \text{ at 10 T, 300 K}$$

$$\mathrm{P} \approx 10^{-5}$$



(a) *n=2*



(b) *n=3*

Approaches to higher sensitivity

$$\xi = \kappa \left(\frac{B_r}{i_r} \right) V_s \omega_0 M = \kappa \left(\frac{B_r}{i_r} \right) V_s \omega_0 P N_s \mu$$

- Better filling factors κ
- Higher polarizations (non-Boltzmann) P
- Alternative detection methodologies
- Pulse sequence engineering

Polarizing NMR

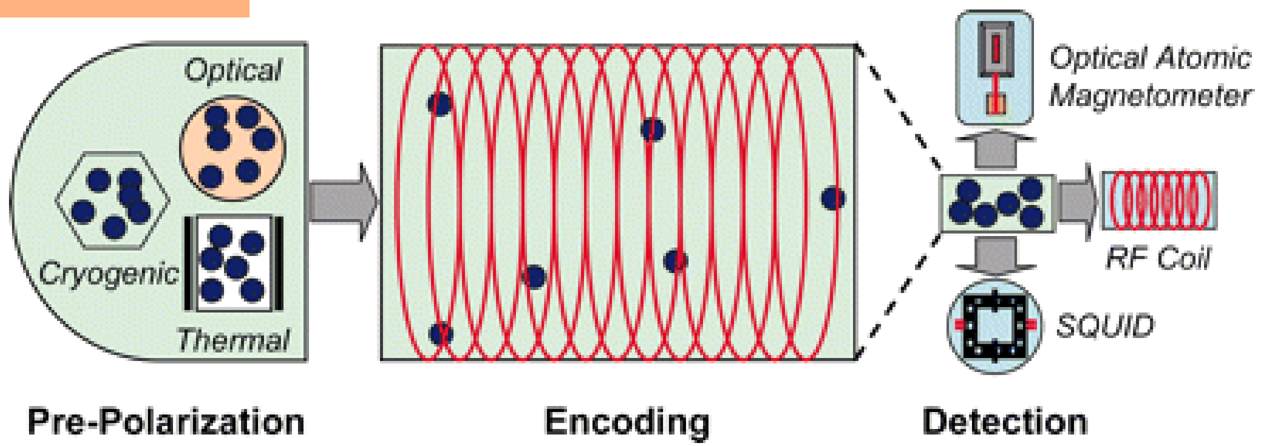
$$\xi = \kappa\left(\frac{B_r}{i_r}\right)V_s\omega_0 M = \kappa\left(\frac{B_r}{i_r}\right)V_s\omega_0 P N_s \mu$$

$$\omega_0 \propto B; P \propto B$$

Make *P* large and independent of *B*.

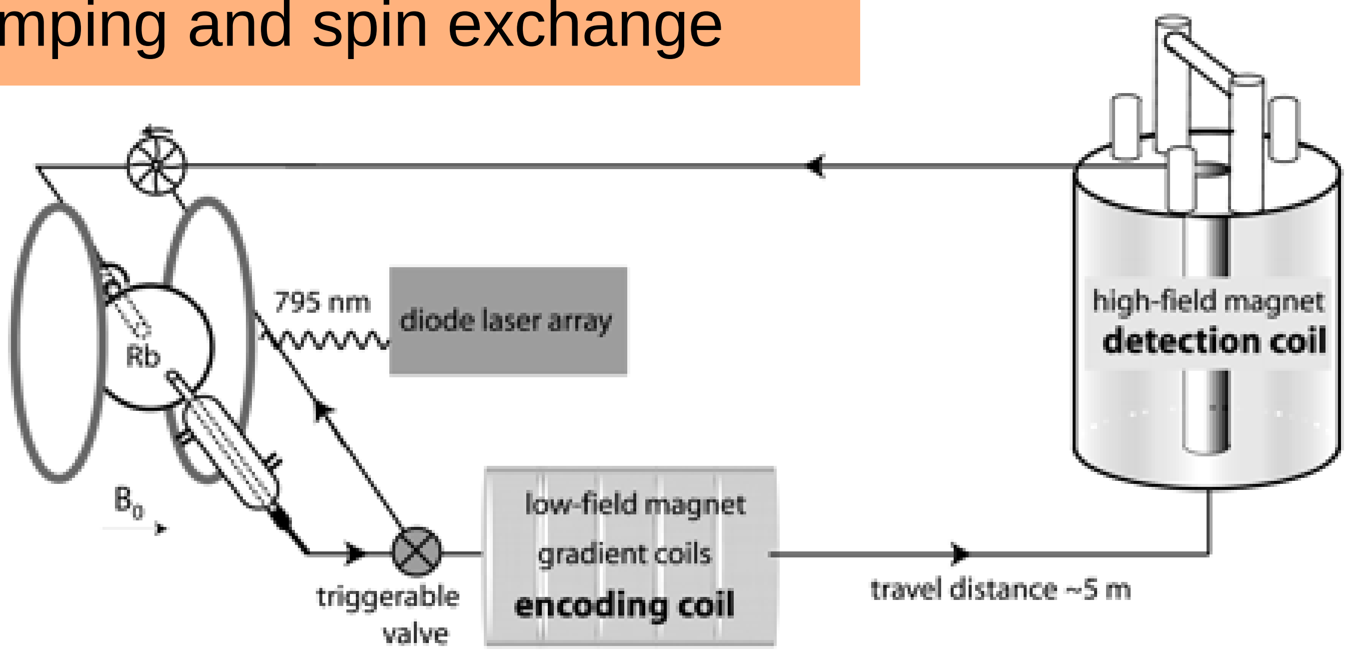
Pre-polarization

X. Xu *et al.*, Proc. Natl. Acad. Sci. 103, 12668-12671 (2006).



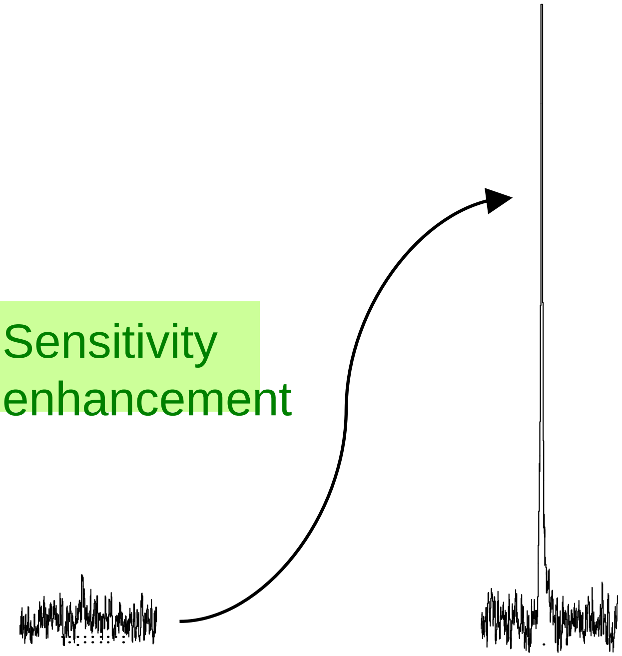
Optical pumping and spin exchange

A.J. Moule *et al.*, Proc. Natl. Acad. Sci. 100, 9122 (2003).

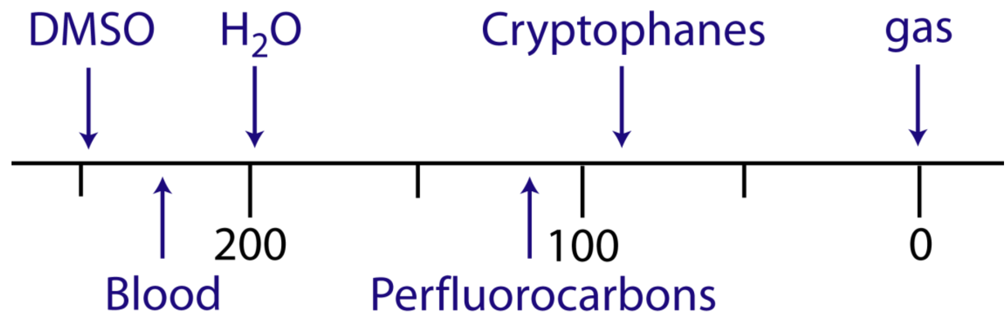


Polarized Xe NMR

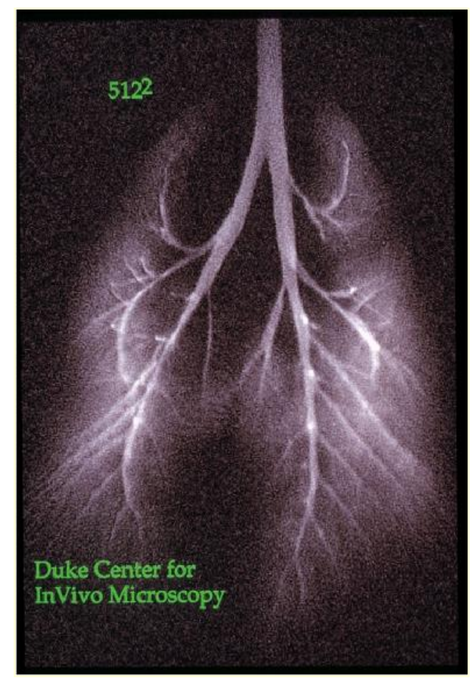
Sensitivity enhancement



thermal polarization   hyperpolarization



Chemical shift range



Polarization through symmetrization

$$|\psi\rangle_T = |\psi\rangle_{ns} |\psi\rangle_r |\psi\rangle_t |\psi\rangle_{vib} |\psi\rangle_e$$

Nuclear spin wavefunctions: Triplets (o-H2)

$$|T_{+1}\rangle = |\alpha\rangle|\alpha\rangle; \qquad |T_{-1}\rangle = |\beta\rangle|\beta\rangle; \qquad |T_0\rangle = \left(|\alpha\rangle|\beta\rangle + |\beta\rangle|\alpha\rangle\right)/\sqrt{2};$$

Singlet (p-H2)

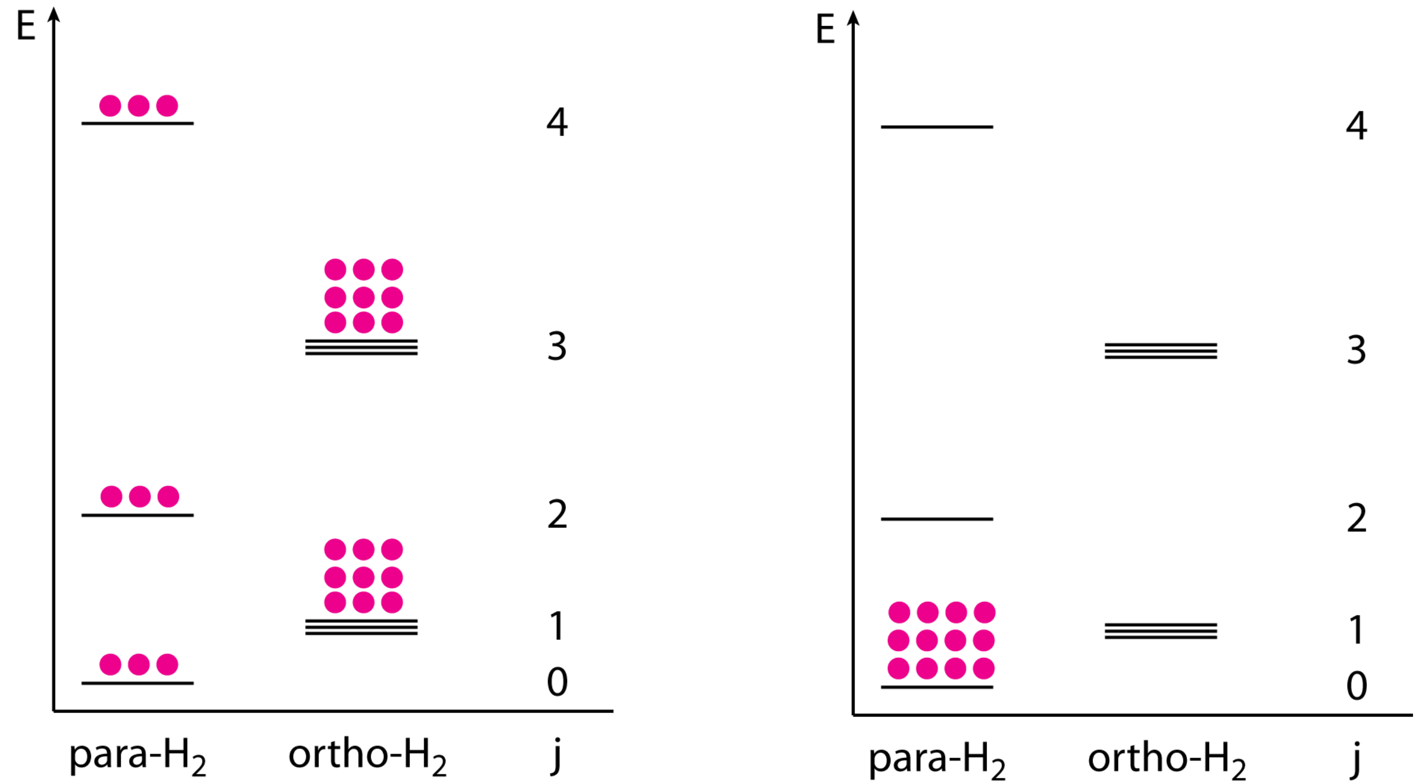
$$|S_0\rangle = \left(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle\right)/\sqrt{2}$$

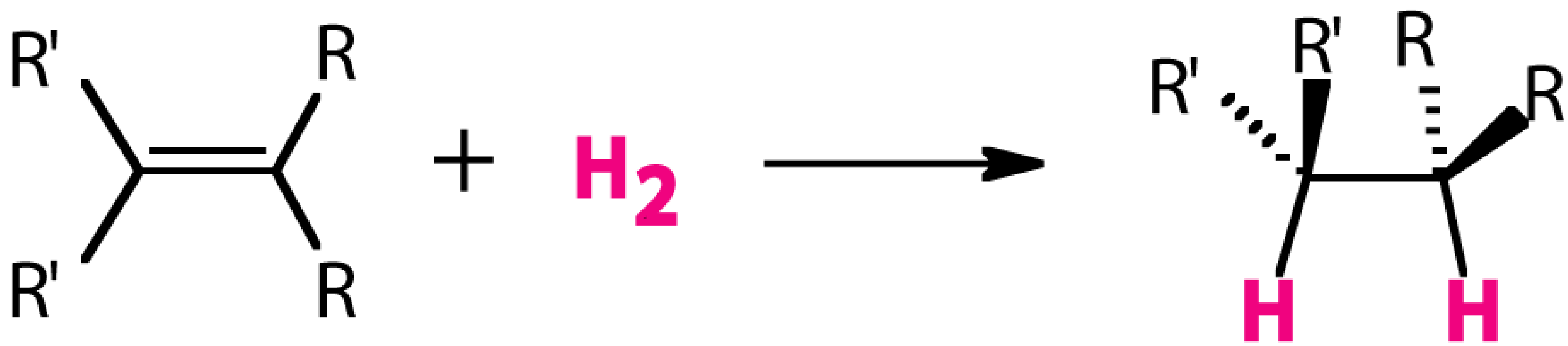
Rotational wavefunction

$$Y^j{}_m(\pi-\theta, \varphi+\pi) = (-1)^j Y^j{}_m(\theta,\varphi)$$

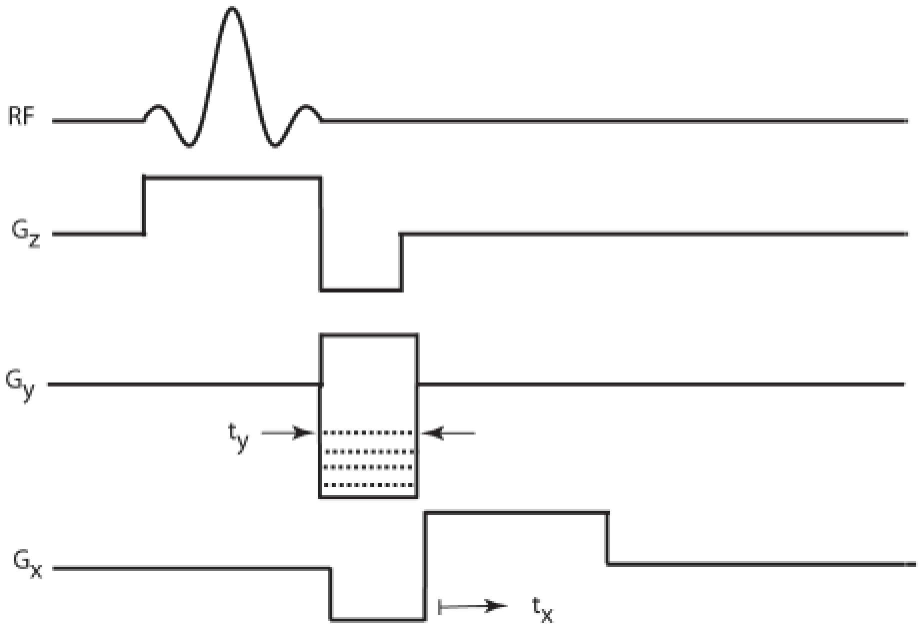
j	$\|\psi>_{rot}$	$\|\psi>_{ns}$	o/p
0	Even	Odd	p
1	Odd	Even	o
2	Even	Odd	p
3	odd	Even	o

Para-Hydrogen





MRI in low magnetic fields



$$\mathbf{B} = B_x(x,y,z)\hat{i} + B_y(x,y,z)\hat{j} + B_z(x,y,z)\hat{k}.$$

$$\frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} + \frac{\partial B_z}{\partial z} = 0, \qquad [29a]$$

$$\frac{\partial B_z}{\partial y} - \frac{\partial B_y}{\partial z} = 0, \qquad [29b]$$

$$\frac{\partial B_z}{\partial x} - \frac{\partial B_x}{\partial z} = 0, \quad \text{and} \qquad [29c]$$

$$\frac{\partial B_y}{\partial x} - \frac{\partial B_x}{\partial y} = 0, \qquad [29d]$$

$$s(t_x, t_y) = \iint_{x,y\,in\,plane} m(x,y)\exp(-i\gamma G_y y t_y)\exp(-i\gamma G_x x t_x)\exp(-i\omega t)\,dx\,dy.$$

$$\mathbf{B}(x,y,z) = B_0\hat{\mathbf{r}} + \left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)\mathbf{B}$$

$$+ \frac{1}{2!}\left(x^2\frac{\partial}{\partial x^2} + y^2\frac{\partial}{\partial y^2} + z^2\frac{\partial}{\partial z^2}\right.$$

$$\left. + 2xy\frac{\partial^2}{\partial x\partial y} + 2yz\frac{\partial^2}{\partial y\partial z} + 2zx\frac{\partial^2}{\partial z\partial x}\right)\mathbf{B} + \ldots.$$

$$\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)\mathbf{B} = \left(x\frac{\partial B_x}{\partial x} + y\frac{\partial B_x}{\partial y} + z\frac{\partial B_x}{\partial z}\right)\hat{i}$$

$$+ \left(x\frac{\partial B_y}{\partial x} + y\frac{\partial B_y}{\partial y} + z\frac{\partial B_y}{\partial z}\right)\hat{j}$$

$$+ \left(x\frac{\partial B_z}{\partial x} + y\frac{\partial B_z}{\partial y} + z\frac{\partial B_z}{\partial z}\right)\hat{k}$$

$$= \begin{pmatrix} G_{(x,x)} & G_{(x,y)} & G_{(x,z)} \\ G_{(y,x)} & G_{(y,y)} & G_{(y,z)} \\ G_{(z,x)} & G_{(z,y)} & G_{(z,z)} \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad [32]$$

The Hamiltonian can be written as,

$$H = H_0 + H_g, \qquad [46]$$

with

$$H_0 = -\gamma\hbar(B_0 I_z) \qquad [47]$$

and

$$H_g = -\gamma\hbar[G_{(x,x)}xI_x + G_{(y,y)}yI_y + G_{(z,z)}zI_z]. \qquad [48]$$

$$H'(t) = G_{(z,z)}zI_z + G_{(x,x)}x[I_x\cos(\omega_0 t) - I_y\sin(\omega_0 t)] + G_{(y,y)}y[I_y\cos(\omega_0 t) - I_x\sin(\omega_0 t)]. \qquad [51]$$

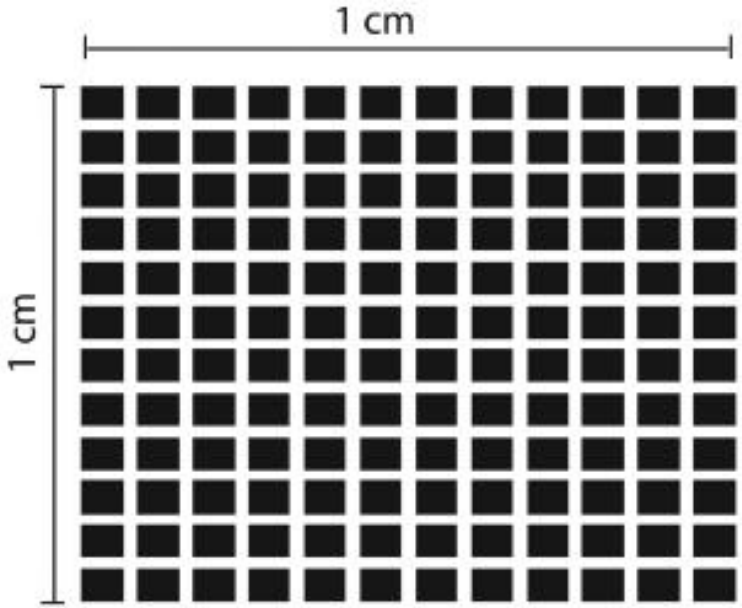
$$\bar{H} = \bar{H}^{(0)} + \bar{H}^{(1)} + \bar{H}^{(2)} + \ldots.$$

$$\bar{H}^{(0)} = \frac{1}{T}\int_0^T H'(t)dt,$$

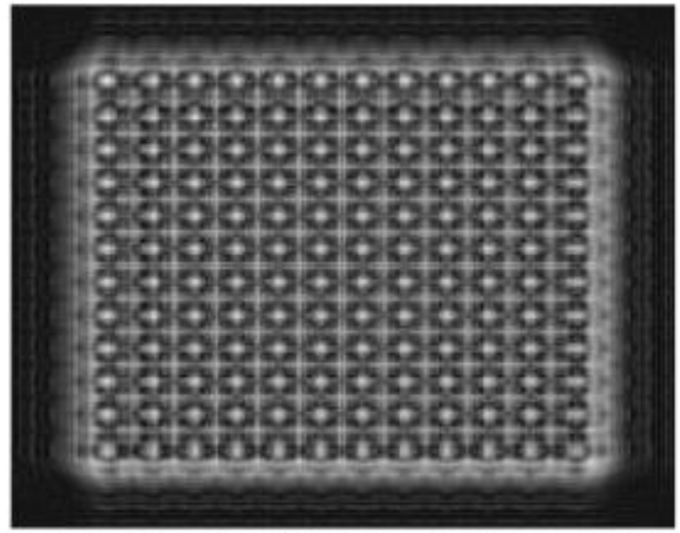
$$\begin{aligned}\bar{H}^{(0)} &= G_{(z,z)}zI_z \\ &+ \frac{1}{T}\Bigg[\int_0^T G_{(x,x)}x(I_x\cos(\omega_0 t) - I_y\sin(\omega_0 t))dt \\ &+ \int_0^T G_{(y,y)}y(I_y\cos(\omega_0 t) - I_x\sin(\omega_0 t))dt\Bigg].\end{aligned}$$

$$\omega_0 \gg \left|G_{(x,x)}x\right|, \quad \left|G_{(y,y)}y\right|,$$

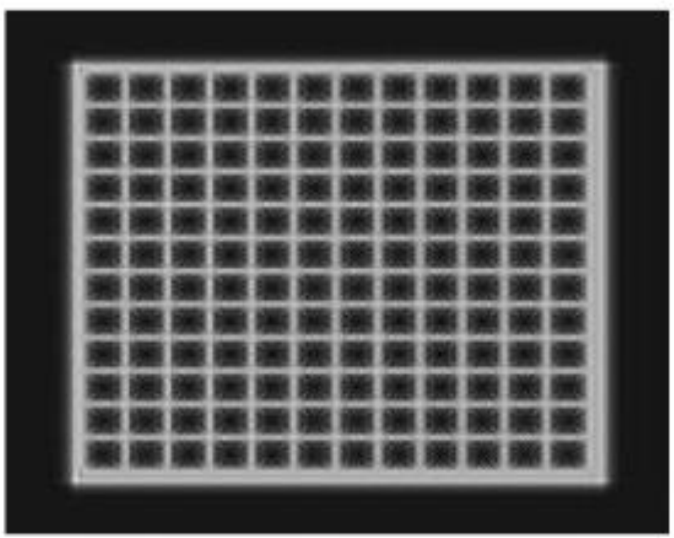
$$\overline{H}^{(0)} = G_{(z,z)}zI_z.$$



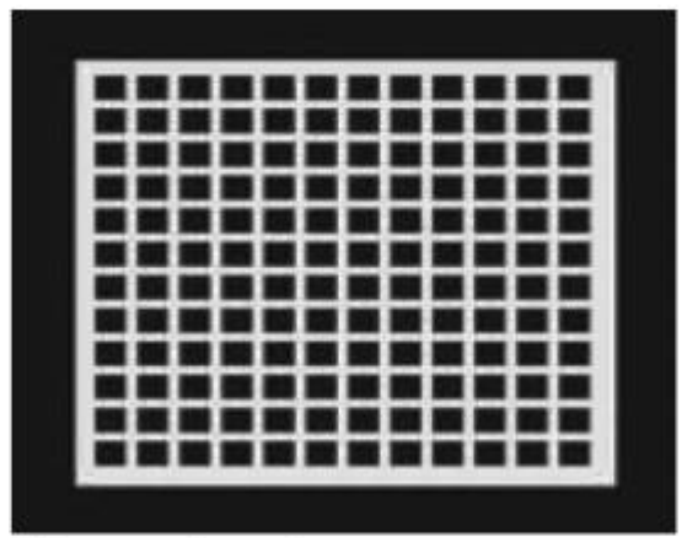
(a) Original Object.



(b) Simulated Image at $B_0 = 10\ \mu T$.



(c) Simulated Image at $B_0 = 100\ \mu T$.



(d) Simulated Image at $B_0 = 500\ \mu T$.