Lecture notes Chem 781 - fall 2008 *© F. Holger Försterling October 16, 2013*

Part 1: Basic Theory:

1.1. Definitions:

Like all other spectroscopic techniques, NMR (**N**uclear **M**agnetic **R**esonance spectroscopy) involves the interaction of the material being examined with electromagnetic interaction. The latter may be characterized by the corresponding range of wavelength λ, frequency ν, and energy *E* :

$\lambda = c/\nu = hc/E$ (h = Plank's constant, c = velocity of light)

The main principle of any spectroscopy: in order for a particle to absorb a photon of electromagnetic radiation, the particle must first exhibit a uniform periodic motion with a frequency that exactly matches the frequency of the absorbed radiation. In terms of quantum mechanics, the energy of the absorbed photon should be equal to an energy splitting of oscillating particles:

$$\Delta E = h\,\nu \quad \textbf{(1.1)}$$

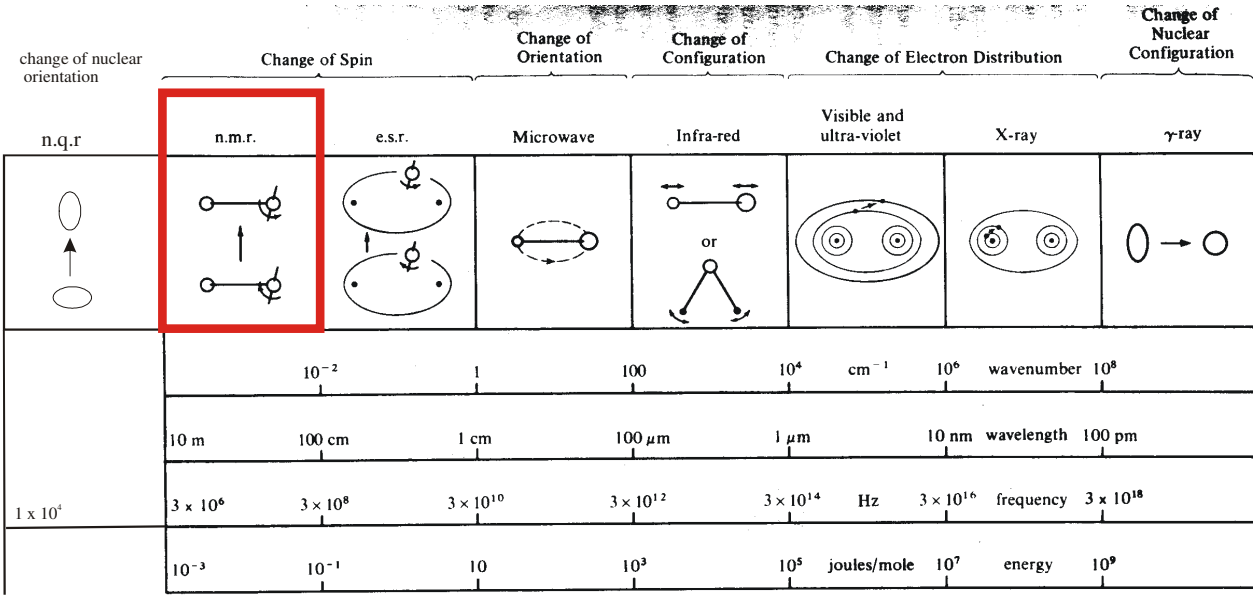


Figure adapted from: C. Banwell, Fundamentals of Molecular Spectroscopy,Third edition,McGraw Hill, London 1983

See table of spectroscopic methods at different frequencies (γ-radiation to radio waves)

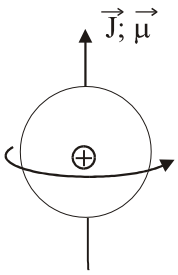
Characteristics of NMR:

- NMR employs radio frequencies (60 - 1000 MHz), it is therefore at the low energy end of spectroscopic methods (NQR is still lower)
- looks directly at the nucleus (change in nuclear spin state) That means we can get an "atom by atom" view of the molecule

- requires external magnetic field: Magnet is one of the most prominent parts of the spectrometer

1.2 Spin angular moment:

Spin is the intrinsic angular momentum of particles. Often it is convenient to visualize the spin of an elementary particle as rotation about its axis resulting in an angular momentum $\mathbf{J}$ (direction of $\mathbf{J}^{\rightarrow}$ is according to right hand rule) . In the case of a charged particle rotation also results in magnetism with a magnetic moment $\vec{\mu}$.



Quantum Mechanics of angular momentum:

Spin angular momentum of an atomic particle has to be treated on a quantum mechanical basis. Analogous to the rotation about a free axis the value of the spin angular momentum can only take multiples of Plancks constant determined by the spin quantum number I:

$$J = \frac{h}{2\pi}\sqrt{I(I+1)} = \hbar\sqrt{I(I+1)} \quad \textbf{(1.6)}$$

Why should spin not be viewed as self rotation of a particle:

One has to keep in mind that this picture of a self rotation of the particle is not correct. On a basic level spin differs from orbital angular momentum, and can not fully explained as classical rotation.

- Elementary particles like the electron can be described as a point like particles and thus there is nothing to rotate. Even regarding them as extended spheres the definition of elementary means there is no way to define points on the surface that move.
- Furthermore using the experimentally maximum possible radius of the electron would require a surface speed larger than the speed of light to achieve the observed angular momentum.
- As opposed to molecular rotation, each particular particle has ***one and only one*** specific spin quantum number, that is an intrinsic constant for each particle and can not be altered.

- Spin quantum numbers an be integer or half integer as shown by experiment. One can show half integer spin quantum numbers can not be derived quantum mechanically from rotations
- Spin appears as necessary property of the wave function when deriving a relavitistic wave function (Dirac equation). The (non relativistic) Schroedinger equation does not contain spin, even though spin can be added empirically to the Schroedinger equation (Pauli matrices)

Examples for particles with different spin quantum numbers:

I = $^1/_2$:electron (e^-), proton (^{1}H), neutron (^{1}n), ^{13}C, neutrino (ν_e)

I = 1 :photon (γ), deuteron (^{2}H) (*I=1 of photon is important for selection rules*)

I > 1 : ^{7}Li ($^3/_2$); ^{17}O ($^5/_2$); ^{59}Co ($^7/_2$)

I = 0 : ^{12}C, ^{16}O

For a list of most important nuclei see handout with table of nuclei with spin and gyromagnetic ratio.

1.3 Magnetic Moment associated with spin

Classical electromagnetism:

A charged particle with angular momentum $\vec{L}$ has a magnetic moment.

Example electron in orbital:

$$\vec{\mu} = -e/(2m_e) \cdot \vec{L} \qquad (\mathbf{1.2})$$

e : elementary charge $\vec{L}$: orbital angular momentum

m_e : mass of electron => *minus sign because of negative charge*

by defining the gyromagnetic ratio $\gamma_l = e/(2m_e)$ one obtains

$$\vec{\mu} = \gamma_l \cdot \vec{L} \qquad (\mathbf{1.3})$$

Electron spin with spin angular momentum $\vec{J}$:

$$\vec{\mu} = g_e \gamma_l \cdot \vec{J} \quad = \gamma_e \vec{J} \qquad (\mathbf{1.4})$$

($g_e \approx 2.0023$ or $\gamma_e = 1.760\ 859\ 770 \cdot 10^{11}$ rad s^{-1} T^{-1})

In this case the experimental magnetic moment differs by the g-factor of the electron from what would be expected by classical electrodynamics. This factor can not be derived from classical electrodynamics nor from the Schrödinger Equation. The relativistic Dirac equation gives exactly g =2. Quantum Field theory adds the remaining 0.0023...

Nuclear spin:

$$\vec{\mu} = g_N \, e/(2m_p) \, \vec{I} = \gamma_N \, \vec{I} \qquad (\mathbf{1.5})$$

with m_p mass of proton.

γ_N is called gyromagnetic ratio of the nucleus, and is a constant specific for each nucleus. (Handout of table of nuclei).

Naively, one would expect $g_N = g_e$. Since mass of a proton m_p much larger than mass of e^- (by a factor of 1861) , γ_p is expected to be a factor 1860 smaller than μ_B, and one would expect $\gamma_p = 9.467 \cdot 10^7$ rad $T^{-1}s^{-1}$. However, neutrons and protons are no true elementary particles, but are composed of quarks, and determination of g_N is not straightforward:

$g_p = 5.7$ for p^+ and $g_n = -3.9$ for neutron resulting in $\gamma_p = 2.67522 \cdot 10^8$ rad $T^{-1}s^{-1}$

and $\gamma_n = -1.8679 \cdot 10^8$ rad $T^{-1}s^{-1}$

The magnetic moment of the neutron can only be understood by its composite nature (according to **1.5** it should be zero as its charge is 0). The more heavy nuclei are composed of protons and neutrons and their total spin angular and magnetic moments are a net effect of both spin and orbital angular momentum of its constituents.

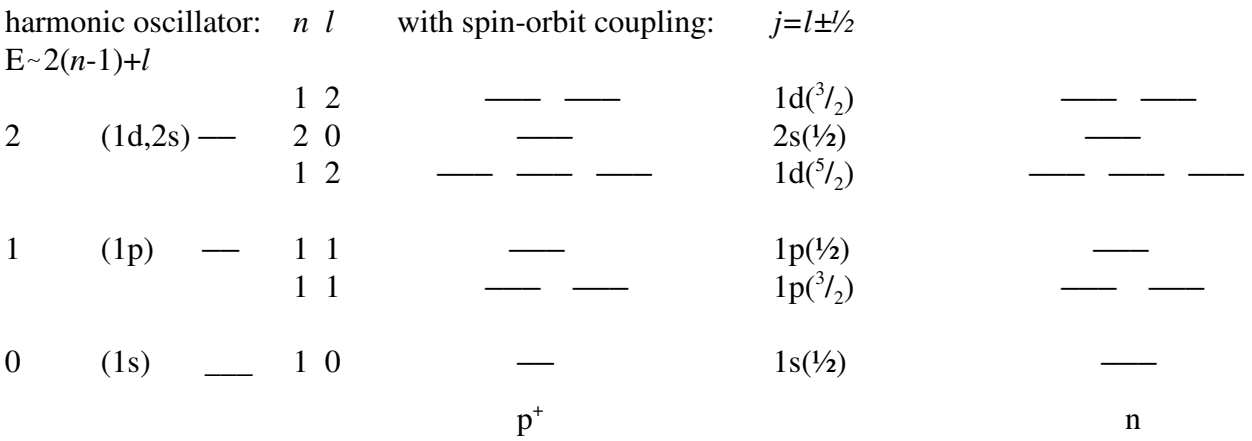
1.4 Spin of complex nuclei

The nuclei of all elements are composed of protons (p^+) and neutrons (n), both of which have I = ½ .

The total spin of a nucleus is a combination of spin- and orbital contributions by its constituents and can be determined by employing the shell model of the nucleus. The Shell model of the nucleus uses energy levels of a modified harmonic oscillator (particle in a spherical box). *Note that the potential is different from the Coulomb potential describing* ***electron*** *orbits around nucleus as we have to regard both coulomb repulsion and nuclear force attraction, the later of which is much less completely understood.* The following rules apply:

- protons and neutrons are initially treated independently with separate energy levels
- A high spin pairing energy results in orbitals filled up one by one (which is the reverse of Hund's rule)
- filled shells (even number of p^+ or n) have zero angular momentum

- for each type of particle the unpaired spin (½) combines with its integer orbital angular momentum (strong spin-orbit coupling), with the higher angular momentum state considerably lower in energy.
- p^+ and n contributions combine to total spin of nucleus



Examples:

Three cases can be distinguished:

- even number of both p^+ and n: all spins paired I = 0
  example: ^{12}C: 6p^+, 6n; ^{16}O: 8p^+, 8n
- even p^+ (n), odd n (p^+): I = $^n/_2$ (half integer)
  ^7Li: 3 p^+, 4n, I = $^3/_2$
  ^{11}B: 5p^+ 6 n => 1 p in 1p($^3/_2$) state: I= $^3/_2$
  ^{13}C: 6p^+, 7n => 1 n in 1p(½) state: I = ½
  ^{15}N: 7 p^+, 8n => 1 p^+ in 1p(½) state: I = ½
  ^{17}O: 8p^+, 9n => 1n in 1d($^5/_2$) state: I = $^5/_2$
  ^{19}F : 9p^+, 10n : I = ½ not obvious
  ^{23}Na: :
  ^{31}P: 15 p^+, 16n: 1p^+ in 2s(½) state: I= ½
- odd p^+, odd n: I = n (integer) ^2H: 1 p^+, 1 n, I = 1; ^{14}N: 7 p^+, 7 n, I = 1;
  ^{10}B: 5 p^+, 5n, I = 3; ^6Li: 3p^+, 3n, I = 1 (!!)

More useful classification for NMR purposes:

I = 0: useless (no NMR signal)

I = ½ : sharp lines because of spherical symmetry of nucleus (the unpaired proton or neutron is in a "s-type" orbital: spherical symmetry, zero orbital momentum, no quadrupole interaction with electric field gradient of surrounding electrons)

I > ½ : often broad lines due to quadrupole interactions (non spherical symmetry of nucleus can interact with non spherical distribution of electrons)

Most of this course will be about spin ½ nuclei (^{1}H, ^{13}C)

1.5. Spins in magnetic field

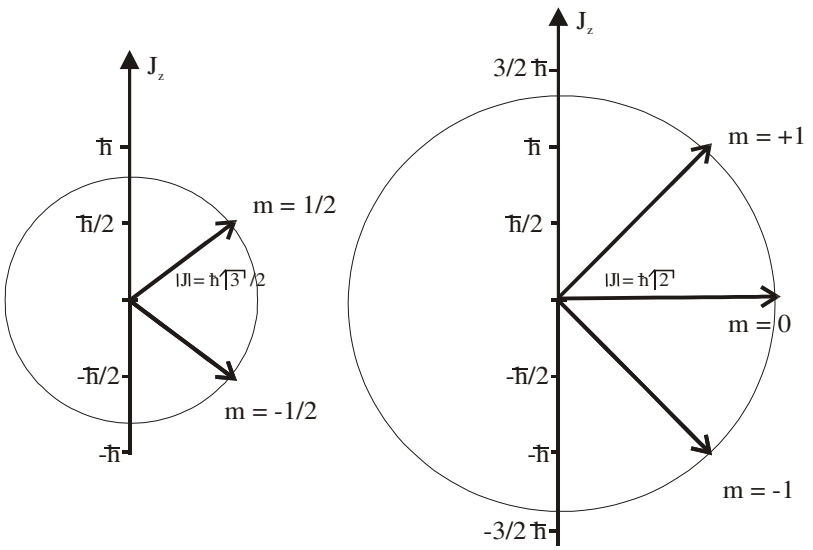
1.5.1. Quantization of spin orientation

In the presence of a magnetic field also the orientation of the angular momentum vector is restricted by an additional magnetic quantum number m_s such that the z-component of the vector is a multiple of $\hbar = {}^{h}/_{2\pi}$:

$$J_z = \hbar m_s \quad \textbf{(1.7a)}; \qquad m_s = -I, -I+1, ..., I-1, I$$

$$\mu_z = \gamma\hbar m_s \quad \textbf{(1.7b)}$$

For a proton (I = ½) that results in two different allowed orientations (m_s = + ½ and m_s = - ½), and three for deuterium (I = 1, m_s = -1, 0 +1), or in general 2 I + 1 allowed orientations.

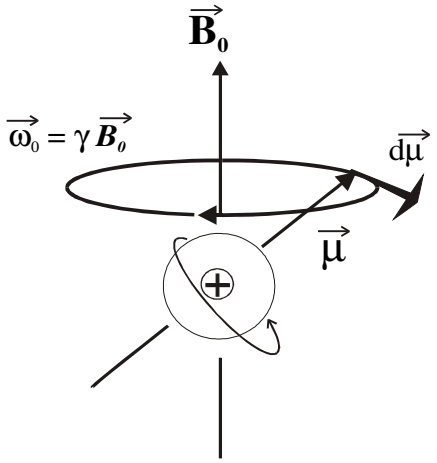


I = 1/2 I = 1

If the z-component is given, the x,y components will be undetermined, and any orientation with that m_z will be possible.

1.5 2. Precession of the magnetic moment vector:

The magnetic quantum number m_s restricts the component of the angular momentum parallel to the magnetic field J_z (and therefore $\vec{\mu}_z$), but not the components perpendicular to the field. That means that the vectors $\boldsymbol{J}$ and $\boldsymbol{\mu}$ can take any orientation on a cone corresponding to a certain value of m_s. From a classical point of view the magnetic field tries to align the magnetic moment parallel to the field. However, like a spinning top or the earth in the suns gravitational field the nucleus is subject to a force perpendicular to $\vec{B}_0$ and $\vec{\mu}$:



$$\frac{d\vec{\mu}}{dt} = \gamma \vec{B}_0 \times \vec{\mu} \quad \textbf{(1.8)}$$

As a result, the nucleus will not align parallel to the field but precess at an angle to the field . This is consistent with the quantum mechanical requirement of restricted values of the z-component of the angular momentum, but no restriction of the x or y component.

The angular velocity of the precession is obtained as

$$\vec{\omega}_0 = -\gamma \vec{B}_0 \qquad or \qquad \nu_0 = \frac{\gamma B_0}{2\pi} \quad \textbf{(1.9)}$$

ω is the angular velocity in rad s^{-1} (angle / s), whereas ν is the frequency measured in s^{-1} (revolutions / s) with $\omega = 2\pi\nu$ (as one revolution = 360° = 2π rad)

The precession frequency **ω_0 is also called the Lamor frequency of a nucleus**.

Exercise: *Precession of a nucleus in the Earth magnetic field, $B_{earth} = 4.7 \cdot 10^{-5}$ T and the field of a typical high field superconducting magnet, 11.75 T:*

Earth magnetic field: $\omega_0 = 4.7 \cdot 10^{-5}\ T \cdot 26.7522\ 10^7\ rad\ T^{-1}\ s^{-1} = 12573\ rad/s$ *or* $\nu_0 = 2\ kHz$

Superconducting magnet: $\omega_0 = 3.13\ 10^6\ rad/s$ *or* $\nu_0 = 500.13\ MHz$ *(field strengths can be expressed by lamor frequencies)*

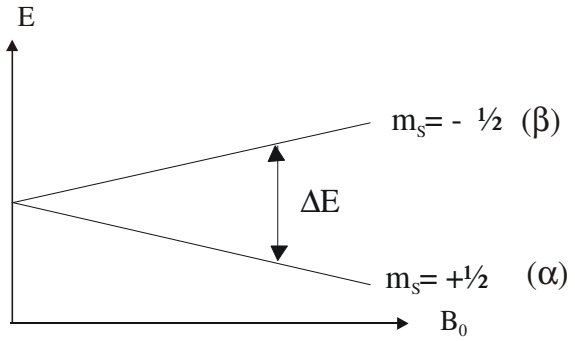
1.5.3 Energy of spin states:

Without external magnetic field, the two orientations of the spin states are degenerate and have the same energy. In the presence of a magnetic field the energies depend on the magnetic quantum number m_s:

$$E_m = -\gamma\hbar \boldsymbol{B}_0\, m_s \qquad \textbf{(1.10)}$$

For a proton that means that the energy of the parallel orientation is lowered and for the anti-parallel it is raised. The transition energy between the two levels $\Delta E = E_{+½} - E_{-½}$ is:

$$\Delta E = \gamma\hbar B_0 = \hbar\omega_0 = h\nu_0 \quad \textbf{(1.11)}$$



ω_0: angular frequency - angle / s (rad s^{-1})

ν_0 : frequency - rotations / s (s^{-1})

Resonance condition for electromagnetic radiation (photons): $h\nu_{RF} = h\nu_0$

Selection Rule: $\Delta m_s = \pm 1$ due to spin 1 of photon

1.6 Magnetization of an ensemble of spins

A macroscopic samples consist of many spins ($6.022 \cdot 10^{23}$ for 1 mol). Due to the difference in energy there is a small excess of the spins aligned with the field ($m_s = +½$) compared to the number of spins aligned in the opposite direction. The probability to find a spin in a certain state is the Boltzmann distribution divided over the total number of states.

$$P^m = \frac{e^{-\frac{E_m}{kT}}}{Z} = \frac{e^{-\frac{m_S\gamma\hbar B_0}{kT}}}{2I+1} \approx \frac{1}{2}\left[1 - \frac{m_S\gamma\hbar B_0}{kT}\right] \qquad \textbf{(1.12)}$$

Z is the partition function which is the sum over all states (weighted by energy):

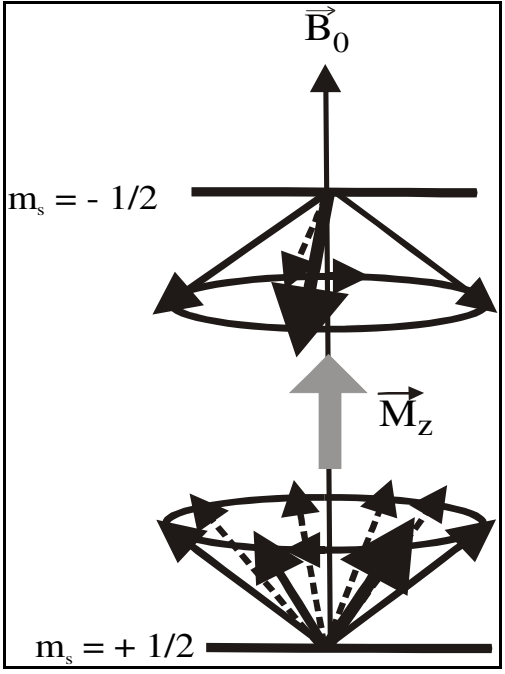
$$Z = \sum e^{-E_m/kT} \quad \textbf{(1.12a)}$$

all m

In the high temperature approximation ($kT \gg \Delta E_m$) Z equals the total number of states or $2I + 1 = 2$ for a spin ½ .

The relative excess in the lower energy level in then given by

$$\frac{\Delta N}{N} = \frac{N^{\alpha} - N^{\beta}}{N} = \frac{N(P^{\alpha} - P^{\beta})}{N} = \frac{\gamma\hbar B_0}{2kT} \quad \textbf{(1.13)}$$



In the earth magnetic field one gets an excess of $3.3 \cdot 10^{-10}$, for a field of 11.75 T 83.16 10^{-6}.

Since the spins are not precessing synchronized they will have random phase (all orientations on the cone have the same probability). Therefore all components of the magnetic moment perpendicular to $\vec{B}_0$ will cancel and only a static z-magnetization aligned with the magnetic field will exist on a macroscopic scale (see figure).

For an ensemble of spin ½ nuclei only the excess spins in the level m_s = + ½ (lower energy) will contribute to the overall magnetization:

$$\vec{M}_z^0 = \Delta N \mu_z^{+\frac{1}{2}} = \frac{\gamma\hbar B_0 N}{2kT}\frac{1}{2}\gamma\hbar = N\gamma^2\hbar^2\frac{N\gamma^2\hbar^2}{4kT}B_0 \quad \textbf{(1.14)} \qquad (I = {}^1/_2)$$

For the more general case of a nuclei of spin I the macroscopic z-magnetization under equilibrium conditions can be obtained as the sum of the contributions from all states:

$$\vec{M}_z^0 = \sum_{m=-I}^{+I} \mu_z^m N^m = N\gamma\hbar \sum_{m=-I}^{I} m P^m \quad \textbf{(1.14a)} \qquad \text{(Any spin I)}$$

Within the high temperature approximation one obtains

Total macroscopic magnetization of many spins

$$\vec{M}_z^0 = N\gamma^2\hbar^2 \frac{I(I+1)}{3kT}\vec{B}_0 \quad \textbf{(1.15)}$$

Curie Law

This general equation applies to all materials containing spins **(Curie Law**). Note that nuclear magnetism is MUCH smaller than paramagnetism or ferromagnetism arising from unpaired electrons, and is normally even weaker than electron induced diamagnetism.

=> In a magnetic field in equilibrium, a constant magnetization of nuclear spins parallel to $\vec{B}_0$ is present (longitudinal magnetization) <=

Observable magnetization M_z^0 will depend on:

- magnetic field B_0: we need as strong magnetic field as possible
- number of spins N, so concentration is important
- square of gyromagnetic ratio γ: one factor due to Boltzmann distribution, one due to dependence of magnetic moment on γ
- inverse temperature T

1.7. Generating x,y (transversal) magnetization:

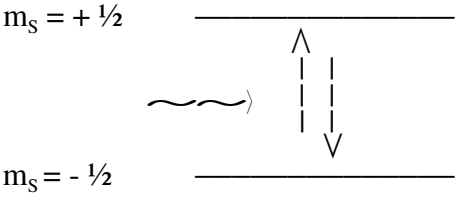
1.7.1. Effect of rf- radiation

Static z-magnetization by itself does not give rise to a signal in the NMR spectrometer. Only magnetization oscillating perpendicular to $\vec{B}_0$ will induce a signal in a receiver coil

=> we need a way perturb the equilibrium and generate x,y magnetization

Quantum mechanical picture:

Irradiate with EM radiation of the frequency according to



$$h\nu = \Delta E = \gamma\hbar B_0 = h\nu_0 \quad \textbf{(1.16)}$$

will stimulate transitions between energy levels (Absorption/Emission). Selection rule for transitions:

$$\Delta m_s = \pm 1$$

(absorption /emission of photon with spin +1)

The effect of RF radiation on macroscopic magnetization can be best understood in a classical vector picture. The coil inside the probe generates an oscillating radio frequency field along x` axis:

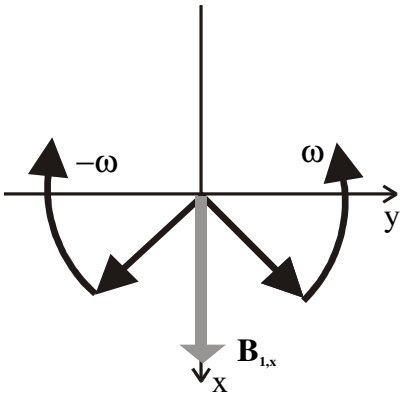
$$\vec{B}_{1,x}(t) = 2\, B_1 \cos(\omega t) \quad (\mathbf{1.17})$$

A linear oscillating magnetic field of amplitude $2B_1$ is equivalent to two counter rotating fields of amplitude B_1. If the resonance condition $\omega_{RF} \approx \omega_0$ is fulfilled, only the component rotating with the lamor precession of will interact with $\vec{\mu}$, the effect of the other component on $\vec{\mu}$ can be neglected as $B_1 \ll B_0$.

If $\omega \approx \omega_0$ the additional B_1 field exerts a torque on M_z and will cause net magnetization **M** to precess $\perp$ to both $\vec{B}_0$ and $\vec{B}_1(t)$ (nutation). Since $B_1 \ll B_0$ only a B_1 field which is synchronized with the lamor precession will be able to have a significant effect on the orientation on **M** : in a sense the $\mathbf{B}_1$ vector will follow the precession of **M** about B_0 and keep $B_1 \perp M$, thus exerting maximum torque at all times. This is like pushing a pendulum in sync with its frequency, even a small push can have a large effect.

As a result the magnetization will be tipped from its initial orientation along the z-axis, while precessing about the static B_0 field. The tip angle θ depends only on the strength of the B_1 field and the amount of time the oscillating field is applied:

$$\theta = \gamma B_1 \tau_P = \omega_1 \tau_P \quad (\mathbf{1.18})$$



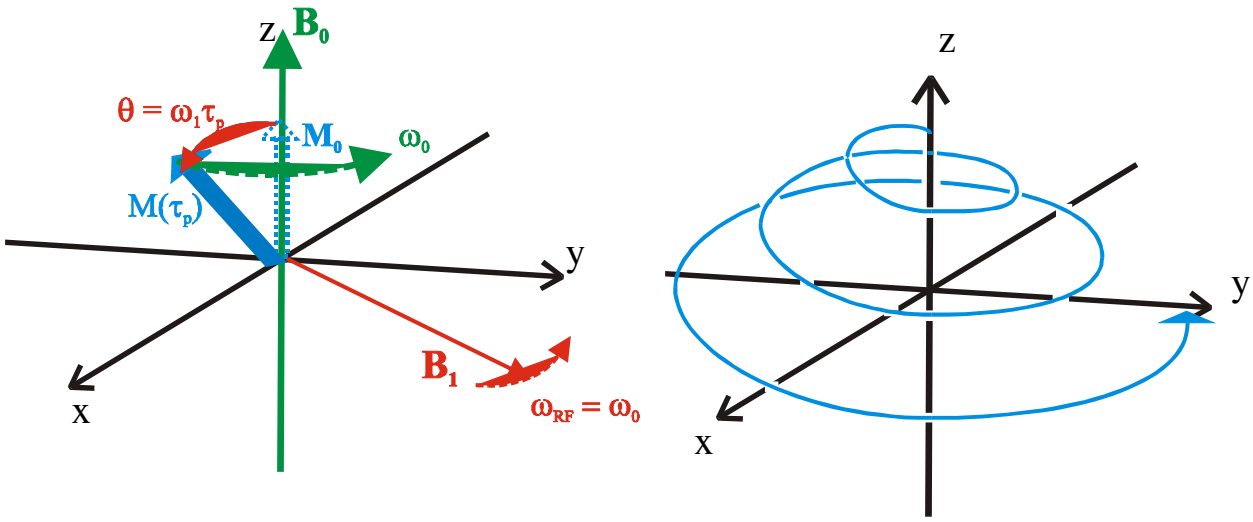


Figure 9: Effect of a B_1 field rotating in the x,y plane with the lamor frequeny $\omega = \omega_0$. Left: Combined precession of the magnetization **M** about $\vec{B}_0$ and the rotating $\vec{B}_1$ field. Right: Trajectory of the magnetization vector during application of a RF pulse.

Note that ω_1 is **NOT** the frequency of the RF field (which is $\omega_{RF} \approx \omega_0$), but the precession of the magnetization about B_1, i.e. the rate of flipping the spins, and is related to the *strength* of B_1.

The result will be the creation of transverse magnetization $M_{x,y}$ as a function of θ:

$$M_{x,y} = M_0 \sin\theta = M_0 \sin(\gamma B_1 \tau_P) \quad \textbf{(1.19)}$$

A maximum of transverse magnetization (and therefore a maximum NMR signal) is observed for $\theta = \pi/2$ (90°) since all of M_z has been converted into $M_{x,y}$. Once the oscillating B_1 field has been turned off the magnetization is precessing freely about B_0, with $\omega_0 = \gamma B_0$ and it is this oscillating magnetization detected in the NMR experiment.

1.7.2 Rotating reference Frame

The complex motion of the magnetization vector can be simplified when the observer is rotating with the B_1 field at the frequency ω_{RF}. This compares to us observing each other on the surface on the earth without worrying about the rotation of the earth about its axis.

In this frame of reference, the B_1 field appears as a static field. Since we are rotating, the precession of the magnetic moments about B_0 will be reduced to $\Omega = \omega_0 - \omega_{RF}$, and will vanish if $\omega_{RF0} = \omega_0$ (on

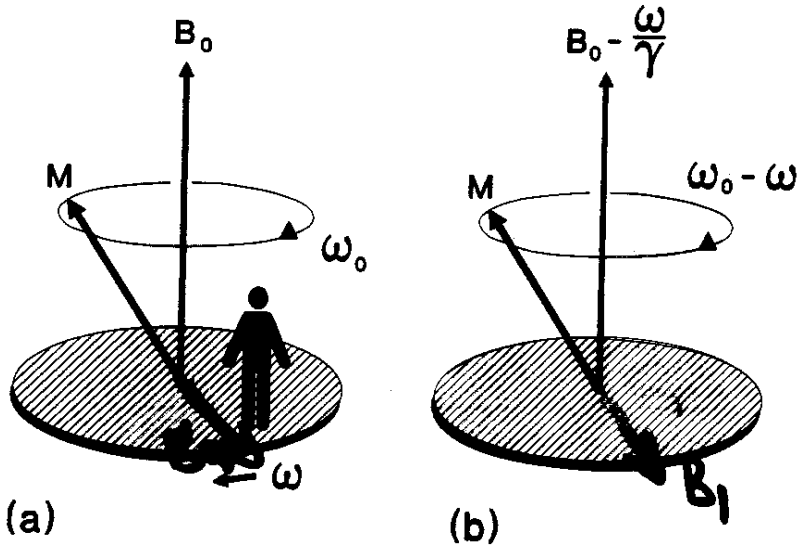


Figure 1.2. Larmor precession as seen in (a) the laboratory reference frame and (b) a rotating reference frame.

resonance). That is equivalent to reducing or removing the effect of the main static magnetic field ($B_0 = 0$).

That results in the following transformations:

Laboratory frame	Rotating frame	Rotating frame on resonance
$\boldsymbol{B}_1(t) = B_{1,x}\cos(\omega t) + B_{1,y}\sin(\omega t)$	$B_{1,x}$	$B_{1,x}$
ω_0	$\Omega = \omega_0 - \omega$	$\Omega = 0$
B_0	$B_0 - \omega_{RF}/\gamma$	0
$\mathbf{B}_{eff} = \boldsymbol{B}_0 + \boldsymbol{B}_1$		$\boldsymbol{B}_{eff} = \boldsymbol{B}_1$
		$\omega_{eff} = \omega_1 = \gamma B_1$

From now on, x and y axes will refer to the coordinates rotating about z with frequency $\omega_{RF} \approx \omega_0$

Analogy: When describing events on earth the coordinate system rotating with the earth is used, not the fixed stars.

1.7.3. Effect of basic pulses

On resonance ($\omega = \omega_0$) the effect of the B_0 field has been removed since the observer rotates with the spins about B_o. Only rotation about $\boldsymbol{B}_1$ field from rf pulse has to be regarded:

=> *Most NMR experiments can be understood on the basis of simple rotations*

$$\frac{d\vec{\mathbf{M}}}{\mathrm{dt}} = \gamma\vec{\mathbf{B}}_1 \times \vec{M} \quad \textbf{(1.20)}$$

Therefore the Magnetization will be rotated perpendicular to $\vec{B}_1$ according to the right hand rule. For a B_1 field along the rotating x axis one obtains:

$$M_z = M_0\, I_z \cos(\omega_1 \tau_P)$$

$$M_x = 0$$

$$M_y = -\, M_0\, I_y \sin(\omega_1 \tau_p)$$

If $\omega_1 \cdot \tau_P = {}^{\pi}/_{2}$ (90° pulse), then after pulse

$M_z = 0$, $M_x = 0$ and $M_y = -M_0$

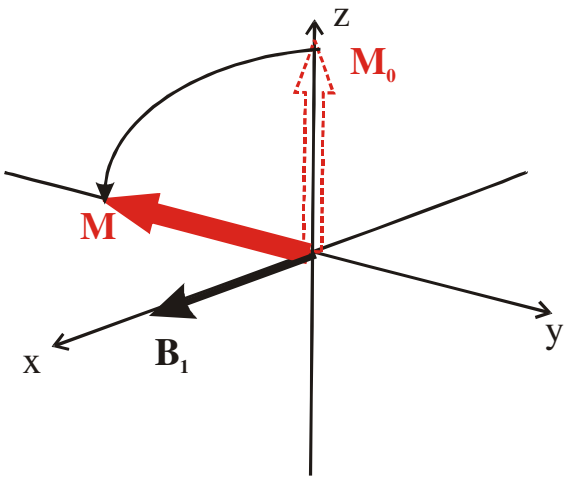


Figure 11: $A({}^{\pi}/_{2})_x$ pulse creates magnetization along -y

For $\omega_1 \cdot \tau_P = \pi$ (180° pulse)

$M_z = -M_0 I_z$, $M_x = M_y = 0$ after the pulse.

That means that a 90° pulse converts all z- magnetization into -y -magnetization, whereas a 180° pulse inverts z- magnetization into -z magnetization.

1.7.4 Off resonance effects

If ω is close, but not exactly on resonance with ω_0, (as in the case of different chemical shifts) there will be precession about the z axis with the frequency $\Omega = \omega_0 - \omega_{RF}$ during the pulse. However as long as the condition $\omega_1 \gg \Omega$ is fulfilled, then this precession will be small. Thus $\boldsymbol{\omega_1 = 2\pi\nu_1 = \gamma B_1}$ is a measure of the bandwidth of excitation:

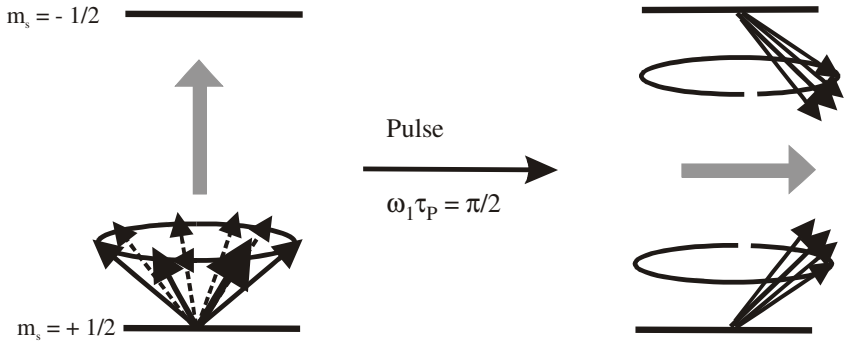
The stronger B_1, the shorter the duration of the pulse τ_P, and the wider the excitation range for which $\omega_1 >> \Omega$.

A typical example: *In a proton spectrum at $\nu_0 = \omega_0/2\pi$ =300 MHz, the typical chemical shift range is 10 ppm, which corresponds to $\Omega_{max} = 2\pi \cdot 3kHz$. For $\omega_1 = 10 \cdot \Omega = 2\pi \cdot 30kHz$, we obtain a duration for a 90 ° rotation (90 degree pulse) of $\tau_P({}^{\pi}/_{2}) = 1/4 \cdot (2\pi)/\omega_1 = 8.3\ \mu s$ which is a typical value.*

With $\Omega_{max}/(2\pi) = 3$ kHz, we obtain an angle of 9 ° of precession during the pulse for signals at the edge of spectrum.

some important consequences of off resonance effects:

- Finite excitation range. Problems can arise in particular in ^{13}C spectra (or other hetero nuclei), where the chemical shift range is much larger, or when multiple pulses have to be applied (and errors will accumulate).
- Phase errors arising from rotation about z- axis during the excitation pulse.
- On the other hand application of very weak pulses (low value of B_1, long $\tau_P(90°)$) will allow for selective excitation (water suppression)



1.7.5 Relation to microscopic quantum mechanical picture:

The macroscopic magnetization is produced by an ensemble of many individual spins:
Without going into the quantum mechanical treatment of the effect of an rf pulse on the spins we can determine from the macroscopic effect that application of radio frequency has two effects: change in population and alignment of the exited spins:

In the case of $\gamma B_1 \tau_P = \pi/2$ (90° pulse) the result is:

- Equal population of α and β spin state: $M_z = 0$
- Excess magnetization becomes aligned along y axis (coherence): $M_y = M_z^0$)

If $\gamma B_1 \tau_P = \pi$ (180° pulse):

- Populations of spin states are inverted (each spin is flipped once) $\bar{M}_z = - M_z^0$
- no alignment in x,y plane, all temporary alignment during the pulse is lost: $M_x = M_y = 0$

1.8. Free precession

If the rotating radio-frequency field $\vec{B}_1$ is turned off, the magnetization is precessing freely about the main field $\vec{B}_0$ with the lamor frequency $\omega_0 = \gamma B_0$.

When viewed in the rotating frame, this amounts to a static magnetization along the -y axis in the "on resonance" case ($\omega = \omega_0$):

$$\vec{\mathbf{M}}_y = -M_0 \vec{\mathbf{I}}_y \quad \text{and} \quad \mathbf{M_x} = 0 \quad \text{for } \omega = \omega_0 \quad \textbf{(1.21)}$$

In the more general case of a $\vec{B}_1$ field not exactly on resonance with ω_0 ($\omega \approx \omega_0$) free precession occurs in the rotating frame with the offset frequency $\Omega = \omega_0 - \omega$:

$$\begin{aligned} \vec{\mathbf{M}}_y &= -M_0 \vec{\mathbf{I}}_y \cos(\Omega t) \\ \vec{\mathbf{M}}_x &= M_0 \vec{\mathbf{I}}_x \sin(\Omega t) \end{aligned} \qquad \textbf{(1.22)}$$

1. 9 Relaxation of signal

The experimentally observed signal is decaying exponentially => rotating x,y magnetization results from NON equilibrium state of sample. System will always restore back to equilibrium state (magnetization along z axis, random phases)

Three cases have to be distinguished:

- dephasing of spins due to differences in lamor frequency (inhomogeneity)
- restoration of equilibrium magnetization (spin-lattice relaxation ≡exchange of energy with lattice)
- random dephasing of spins (Spin-spin relaxation)

Signal decay through inhomogeneity :

In real sample: Field is not perfectly homogeneous. Spins in different parts of sample will experience a different field => different ω_0

result: aligned spins will dephase with time and macroscopic x,y magnetization will eventually vanish.

The effects effect of linear vs. square and higher order gradients in the field are mentioned in lab

Important: Inhomogeneity dephasing is reversible if field gradient or orientation of spins is reversed

Situation is like different chemical shifts. Spins within small subvolumes are still aligned and precessing with one particular frequency.

Spin-lattice relaxation (relaxation of z-magnetization):

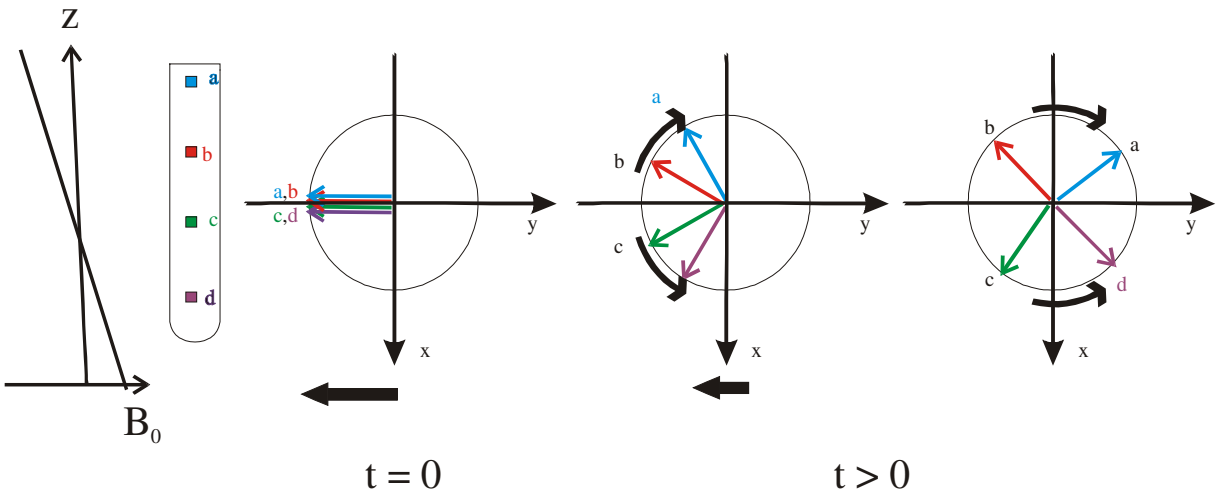
population of energy levels will return to equilibrium levels (thermal equilibrium) and reestablish z-magnetization. This is called longitudinal relaxation (time constant T_1). All processes contributing to longitudinal relaxation (T_1)will also contribute to a corresponding reduction of transverse (x,y) magnetization (T_2, see below) => buildup of z magnetization on expense of x,y magnetization

Spin-spin relaxation (relaxation of x,y magnetization):

Even in perfectly homogeneous B_0 field x,y magnetization will decay: Reason interaction of nuclei with lattice **AND** each other. In addition to random transitions to reestablish equilibrium z magnetization with the time constant T_1, spin spin interactions (chemical exchange, spin diffusion, dependence of ω_0 on orientation) can result in dephasing of spins without change in population energy levels. Result is *random* (statistical) change in phase => irreversible (Entropy)

The relaxation of x,y magnetisation is described by time constant T_2 (transversal relaxation)

It is always $T_1 \geq T_2$



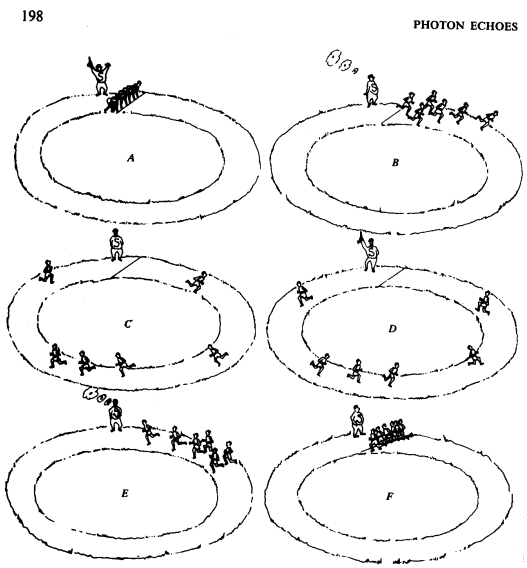


Fig. 9.2 Dephasing and reversal on a race track, leading to coherent rephasing and an "echo" of the starting configuration. [From *Phys. Today*, front cover, November 1953. Reproduced by permission.]

The difference between inhomogeneity broadening and T_2 relaxation can be visualized by runners on a track: Different individuals have different speed and at some point all runners will be equally distributed around the track. But if they reverse direction they will meet all again in the same location. In real life runners will not have the same speed throughout the run, so they will be more out of sync when meeting up than at the start => T_2 dephasing
Any runner dropping out of the race (T_1) will also contribute to the reduction of the signal and T_2.

The experimentally observed decay of NMR signal is a combined effect of inhomogeneity broadening and transversal relaxation with time constant T_2^*

with $1/T_2^* = \gamma\Delta B_0/2 + 1/T_2$ where ΔB_0 is the maximum spread of field values.

The line width is given by the decay rate of the signal, it is

$$\Delta\nu_{1/2} = 2/(\pi T_2^*) \qquad \textbf{(1.23)}$$

Considering free precession and relaxation, the three components of the magnetization present after a 90° pulse along x can be described as follows:

$$\begin{aligned} \vec{\mathbf{M}}_z &= M_0\vec{\mathbf{I}}_z[1-e^{-\frac{t}{T_1}}] \\ \vec{\mathbf{M}}_y &= -M_0\vec{\mathbf{I}}_y\cos(\Omega t)\ e^{-\frac{t}{T_2^*}} \\ \vec{\mathbf{M}}_x &= M_0\vec{\mathbf{I}}_x\sin(\Omega t)\ e^{-\frac{t}{T_2^*}} \end{aligned} \qquad \textbf{(1.24)}$$

Bloch Equations of free precession in a magnetic field after a 90 °$_x$ pulse ($M_z(t=0)=0$, $M_x(t=0)=0$, $M_y(t=0)=-M_o I_y$)

Implications of signal decay by T_2^* for experiment:

- Maximizing the homogeneity will improve the resolution of the experiment (longer T_2^* and therefore smaller $\Delta\nu$. Sensitivity will also be improved (why ?)
- Acquisition time must be long enough for signal to decay to zero in order to avoid artefacts. This is often not possible in 2D experiments -> sine or qsine filter functions have to be applied before processing
- Extending acquisition time beyond $\approx 3\ T_2$ will not accumulate any more signal

Implications of finite recovery time T_1

- one scan: 90° excitation pulse will give maximum signal. If many scans are to be accumulated, one will have to wait for z-magnetization to recover between scans (normally $5 \cdot T_1$ for full recovery). With $T_1 \approx 1$ - 5s for protons this is very time consuming. Often it is more advantageous to excite with shorter pulses and use shorter repetition time. The optimum pulse angle is called Ernst Angle

$$\theta_E = \exp(T_R/T_1) \qquad (\mathbf{1.25})$$

T_R = aq + d1 repetition time

- for quantitative determinations intensity (more accurate: integral) will only be meaningful if same z-magnetization was present before each pulse for each species. If multiple scans are added, repetition time needs to be $5\ T_1$(max) for accurate results.
- After inserting sample into magnet it will take a few seconds for magnetization to build up. Normally no problem. But some low γ nuclei (^{103}Rh) or isolated spins ($CHCl_3$ in degassed, deuterated solvent) can have T_1 of several minutes.

<u>Exercise:</u> a) Generalize the Bloch equation for free precession after an arbitrary pulse width θ

b) What are the relationships for a sample just inserted into the magnet ?

Further Reading:

General Textbooks:

- J.W. Akitt, NMR and Chemistry, fourth ed. Chapter 1
- Andrew Derome, Modern NMR techniques for Chemistry Research, Chapter 4.1 - 4.3.3 and 4.4-4.4.3
- Harald Günther**,** NMR Spectroscopy, second ed. Chapter 1, Chapter 7, pp221-233
- Edwin Becker, High Resolution NMR: Theory and Chemical Applications, Third Ed; Chapter 2.1 - 2.9
- Jeremy Sanders, Brian Hunter; Modern NMR Spectroscopy; second Ed. ; Ch. 1.1-1.2.5 and 1.2.7
- Frank van de Ven; Multidimensional NMR in Liquids; Ch. 1.1 - 1.4

Nuclear Shell Model:

- G. Friedlander et al.; Nuclear and RadioChemistry, 3rd Ed.; Ch. 10.D
- http://en.wikipedia.org/wiki/Shell_model
- http://www.hep.phys.soton.ac.uk/hepwww/staff/D.Ross/phys3002/shell.pdf