Introduction to Nuclear Magnetic Resonance Spectroscopy

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1.1. Introduction to Magnetic Resonance

- Magnetic resonance (MR) is a phenomenon of resonant energy absorption by a system of nuclei (and electrons).
- Nuclear magnetic resonance (NMR) results from the intrinsic magnetic moment of the nuclei of some atoms. Magnetic moments of electrons are exploited in electron spin resonance (ESR).
- Magnetic resonance (MR) generally involves placing a sample in a strong magnetic field (to generate polarisation at a fixed resonant frequency) and detecting signals produced following application of pulsed radio-frequency electromagnetic fields (RF pulses).
- MR is a very powerful method for studying the structure of materials: used in physics, chemistry, biology, medicine etc.

- NMR spectroscopy is used for chemical analysis and for molecular structure determination

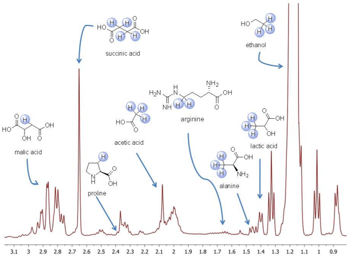

Fig.1: [1]H NMR spectrum of a sample of Spanish wine (`http://www.unirioja.es/gsoe/NMR.htm`)

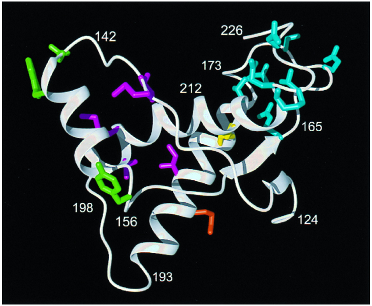

Fig.2: NMR-derived structure of a prion `http://www.pnas.org/content/94/14/7281.full`

- NMR relaxometry can be used to monitor molecular environment

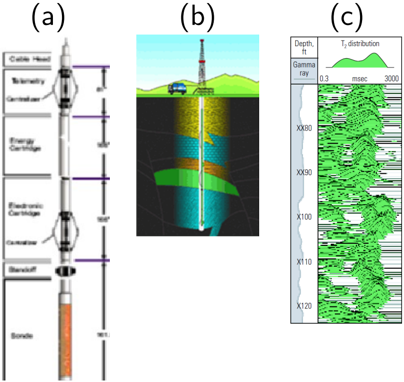

Fig.3: (a) NMR-logging probe, (b) Schematic positioning of the probe in a well, (c) T_2-relaxation profile along the bore. Sources: 1) Allenet al. Oilfield review, Autumn 2000; 2) Coates, Xiao NMR Logging Principles and Applications, Hulliburton

- NMR forms the basis for magnetic resonance imaging (MRI)

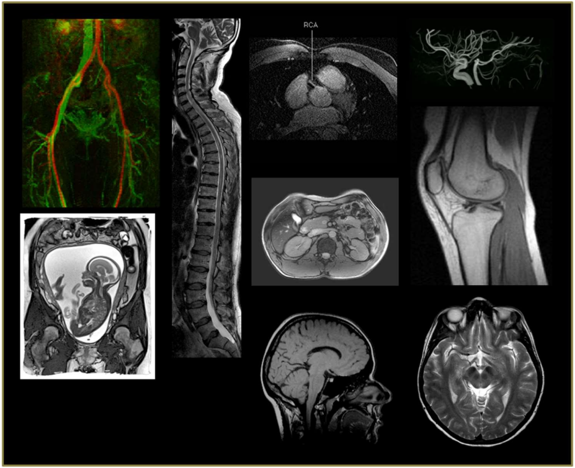

Fig.4: Example magnetic resonance images of blood vessel (in legs), fetus in utero, spine, heart, abdomen, head, blood vessels (in brain), knee, brain (courtesy of Prof. Richard Bowtell)

1.3. Magnetic moments in magnetic field.

- Consider charges moving in a limited volume. The position of a charge $\mathbf{e_n}$ will be given by a vector $\mathbf{r_n}$ and its velocity by $\mathbf{v_n}$. The overall magnetic moment of such a system is defined as:

$$\mathbf{M} = \frac{1}{2} \sum_n e_n \mathbf{r_n} \times \mathbf{v_n} \tag{1}$$

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- If all the charges and masses are the same, then $\mathbf{M}$ can be rewritten as:

$$\mathbf{M} = \frac{e}{2m}\sum_n m\mathbf{r_n} \times \mathbf{v_n} = \gamma \mathbf{L}, \tag{2}$$

where

$$\mathbf{L} = \sum_n \mathbf{p_n} \times \mathbf{r_n} \tag{3}$$

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- Gyromagnetic ratio (or magnetogyric):

$$\gamma = \frac{e}{2m} \tag{4}$$

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$$E = -\mathbf{M} \cdot \mathbf{B} \tag{5}$$

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- Now using equation 2 we can obtain the equation describing the motion of vector **M**:

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \tag{7}$$

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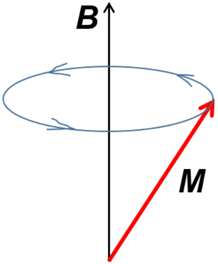
- In a uniform magnetic field directed along z-axis $\mathbf{B} = (0, 0, B_0)$, the equation for individual components of $\mathbf{M}$ follow the equations:



$$\frac{dM_x}{dt} = \omega_L M_y$$
$$\frac{dM_y}{dt} = -\omega_L M_x \qquad (8)$$
$$\frac{dM_z}{dt} = 0,$$

where $\omega_L = \gamma B_0$ - Larmor frequency.

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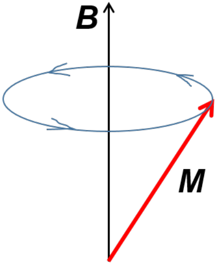

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where $\omega_L = \gamma B_0$ - Larmor frequency.

- A solution to this system of differential equations with initial values of $M_x(0), M_y(0), M_z(0)$ has the following form:

$$\begin{aligned} M_x(t) &= M_x(0)\cos(\omega_L t) + M_y(0)\sin(\omega_L t) \\ M_y(t) &= -M_y(0)\sin(\omega_L t) + M_y(0)\cos(\omega_L t) \\ M_z(t) &= M_z(0) \end{aligned} \qquad (9)$$

- In quantum mechanics physical quantity A ise represented by an operator $\hat{A}$. The mechanical angular momentum is replaced by its corresponding operator:

$$\mathbf{L} = \sum_n \mathbf{p_n} \times \mathbf{r_n} \longleftrightarrow \hat{\mathbf{L}} = \frac{1}{\hbar} \sum_n \hat{\mathbf{r}}_\mathbf{n} \times \hat{\mathbf{p}}_\mathbf{n} = -i \sum_n \hat{\mathbf{r}}_\mathbf{n} \times \boldsymbol{\nabla}_\mathbf{n} \quad (10)$$

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- Angular momentum operator properties. Commutation:

$$[\hat{L}_y, \hat{L}_z] = i\hat{L}_x, [\hat{L}_z, \hat{L}_x] = i\hat{L}_y, [\hat{L}_x, \hat{L}_y] = i\hat{L}_z \quad (11)$$

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- Angular momentum squared, and its commutation properties:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (12)$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \quad (13)$$

1.4. Orbital angular momentum operator

- Eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$ operators can be characterized by integer quantum numbers l and m respectively. These eigen functions will be denoted as $|lm\rangle$. Their eigenvalues are:

$$\hat{L}_z|lm\rangle = m|lm\rangle \tag{14}$$

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- Another useful operator are raising and lowering operators:

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \hat{L}_- = \hat{L}_x - i\hat{L}_y \tag{16}$$

$$\langle lm|\hat{L}_+|l(m-1)\rangle = \langle l(m-1)|\hat{L}_-|lm\rangle = \sqrt{(l+m)(l-m+1)} \tag{17}$$

Problem

Calculate $[\hat{L}_+, \hat{L}_x] =?$, $[\hat{L}_+, \hat{L}_-] =?$

$$[\hat{L}_y, \hat{L}_z] = i\hat{L}_x, [\hat{L}_z, \hat{L}_x] = i\hat{L}_y, [\hat{L}_x, \hat{L}_y] = i\hat{L}_z$$

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- Classical magnetic moment will have its own quantum analogue, the operator of angular momentum:

$$\mathbf{M} = \gamma \mathbf{L} \longleftrightarrow \hat{\boldsymbol{\mu}} = \gamma \hbar \hat{\mathbf{L}} \tag{18}$$

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- Given the electron charge $e = 1.6 \cdot 10^{-19}$C, and mass $m = 9.1 \cdot 10^{-31}$kg Bohr magneton:

$$\beta_e = \gamma \hbar = \frac{e\hbar}{2m} \approx 9.27 \cdot 10^{-24} \mathrm{J{\cdot}T}^{-1} \tag{19}$$

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- Similarly a nuclear magneton could be calculated for a proton (^{1}H nucleus):

$$\beta = \gamma_N \hbar = \frac{e\hbar}{2m_p} \approx 5.05 \cdot 10^{-27} \mathrm{J{\cdot}T}^{-1} \tag{20}$$

However, real nuclei and electrons have spins (intrinsic magnetic moment). Their z-axis projection m takes integer and half-integer values: $m = \frac{1}{2}, 1, \frac{3}{2}, 2$ etc. Similar to the equation for the orbital angular momentum Eq.18. For nuclei spins we get its magnetic moment as:

$$\hat{\boldsymbol{\mu}}_{\mathbf{N}} = \gamma_N \hbar \hat{\mathbf{I}}, \tag{21}$$

where $\hat{\mathbf{I}}$ stands for the nuclear spin operator. All the properties of angular momentum operators listed in Eqs.11-17 will be true for $\hat{\mathbf{I}}$.

- Many nuclei in the periodic table are magnetic, i.e. have spin $I \neq 0$. Their magnetic moments could be measured in units of β_N:

$$\hat{\boldsymbol{\mu}}_{\mathbf{N}} = \gamma_N \hbar \hat{\mathbf{I}} = g_N \beta_N \hat{\mathbf{I}}, \tag{22}$$

where g_N - dimensionless g-factor.

1.5. Spin angular momentum operator

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^1H	99.98	$\frac{1}{2}$	5.585	26.7519
^2H	$1.5*10^{-2}$	1	0.857	4.1066
^{13}C	1.108	$\frac{1}{2}$	1.405	6.7283
^{14}N	99.635	1	0.403	1.9338
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- Electron magnetic moments can be measured in units of Bohr magnetons: $\hat{\boldsymbol{\mu}}_{\mathbf{S}} = -\gamma_e \hbar \hat{\mathbf{S}} = -g_e \beta_e \hat{\mathbf{S}}$, and for a free electron spin $g_e \approx 2.0023$.

Summary of Lecture 1

- Applications of NMR: chemistry, biology, medicine, industry ...
- Magnetic moment in magnetic field: Classical description
- Recap of angular momentum operator properties: commutation properties.
- Nuclei have their own nuclear magnetic moment. Described using spin angular momentum operator.

Suggested reading: Harris: 1.1, 1.2, 1.3, 1.4, 1.6, 2.4

- Let's quantum mechanically describe the system of spins in the magnetic field. Eq. 5 can be rewritten in a form of Hamiltonian:

$$E = -\mathbf{M} \cdot \mathbf{B} \longleftrightarrow \mathcal{H} = -\hat{\mu}_{\mathbf{N}} \cdot \mathbf{B} \tag{23}$$

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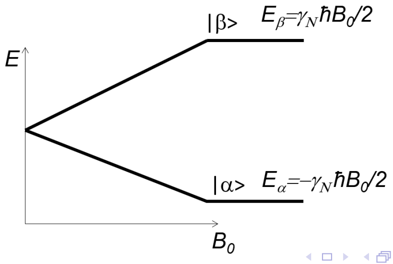
- For spin $I = \frac{1}{2}$ such Hamiltonian produces a two-level system. Its energy levels corresponding to eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$:



- The transition between the two states requires an energy quantum[1]:

$$h\nu_L = \gamma\hbar B_0, \omega_L = \gamma B_0, \nu_L = \frac{\gamma B_0}{2\pi} \tag{25}$$

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^{13}C	1.108	$\frac{1}{2}$	125.721	6.7283
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^{15}N	0.365	$\frac{1}{2}$	50.664	-2.712

1.7. Equilibrium magnetization

NMR measurements are generally made on bulk samples which contain very large numbers of nuclear spins (e.g. 1 cm^3 contains $N \approx 6.7 \cdot 10^{22}$ ^1H atoms) The measured signals therefore result from the collective effect of a large number of magnetic moments that can be described using a bulk magnetization. At thermal equilibrium, the numbers of nuclei in the $|\alpha\rangle$ state N_α and $|\beta\rangle$ state N_β follow Boltzmann distribution:

$$\frac{N_\alpha}{N_\beta} = e^{-\frac{\gamma B_0}{kT}} \approx (1 - \frac{\gamma B_0}{kT}), \tag{26}$$

when $\gamma B_0 \ll kT$. Overall magnetization then can be calculated as:

$$M_z = N_\alpha(-\frac{1}{2}\gamma\hbar) + N_\beta(\frac{1}{2}\gamma\hbar) = N\frac{\gamma^2\hbar^2 B_0}{4kT} \tag{27}$$

Problem

- What is the value of $\dfrac{\gamma_N \hbar B_0}{kT}$ for proton nuclei (^{1}H) at 9.4 T magnetic field at 300 K?
- What is the value of $\dfrac{\gamma_e \hbar B_0}{kT}$ electron (^{1}H) at 9.4 T magnetic field at 4 K?

Electron charge $e = 1.602 \cdot 10^{-19}$C

Electron mass $m_e = 9.109 \cdot 10^{-31}$kg

Proton mass$m_p = 1.673 \cdot 10^{-27}$kg

Plank constant$\hbar = 1.054 \cdot 10^{-34} \dfrac{\mathrm{J} \cdot \mathrm{s}}{rad}$

Proton g-factor$g_p = 5.585$

Electron g-factor$g_e = 2.0023$

Nuclear magneton$\beta_N = 5.05 \cdot 10^{-27}\mathrm{J} \cdot \mathrm{T}^{-1}$

Bohr magneton$\beta_e = 9.27 \cdot 10^{-24}\mathrm{J} \cdot \mathrm{T}^{-1}$

Proton gyromagnetic ratio$\gamma_N = 26.7519 \cdot 10^7 \dfrac{\mathrm{rad}}{T \cdot s}$

Electron gyromagnetic ratio$\gamma_e = 1.76 \cdot 10^{11} \dfrac{\mathrm{rad}}{T \cdot s}$

Boltzmann constant$k = 1.38 \cdot 10^{-23}\mathrm{J} \cdot \mathrm{K}^{-1}$

Avogadro's constant$N_A = 6.023 \cdot 10^{23}\mathrm{mol}^{-1}$

1.8. Resonant energy absoption.

- Let's apply oscillating magnetic field to our system. A spin system Hamiltonian becomes time-dependent and for an oscillation along the x-axis we obtain:

$$\begin{aligned} \mathcal{H}(t) &= -\hat{\boldsymbol{\mu}}(\mathbf{B_0} + \mathbf{B(t)}) = \\ &= -\gamma\hbar\hat{I}_z(B_0 + B_1(t)) = \\ &= -\gamma\hbar\hat{I}_z B_0 - \gamma\hbar\hat{I}_x B_1 \cos(\omega t), \end{aligned} \tag{28}$$

where H_1 and ω are the amplitude and the frequency of the oscillating magnetic field.

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  where H_1 and ω are the amplitude and the frequency of the oscillating magnetic field.

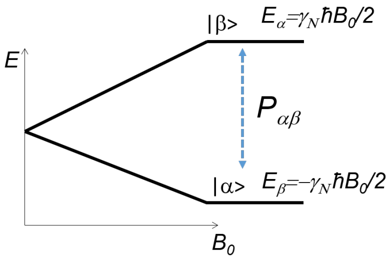
- According to perturbation theory the transition probability between the initial state $|a\rangle$ and the final state $|b\rangle$ with a time dependent Hamiltonian $\hat{V}(t) = 2\hat{F}\cos(\omega t)$ is (Fermi's golden rule):

$$P_{ab} = \frac{2\pi}{\hbar}|\langle a|\hat{F}|\rangle b|^2 \delta(E_{ab} - \hbar\omega), \quad (29)$$

  where $E_{ab} = E_a - E_b$ is an energy difference between the energies of levels a and b.

- For a two level system described before, the matrix element $\langle\alpha|\hat{I}_x|\beta\rangle = \frac{1}{2}$. The transition probability then becomes:

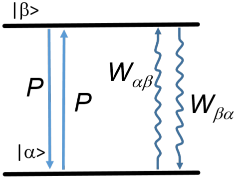
$$P_{\alpha\beta} = \frac{\pi}{2\hbar}(\gamma H_1)^2\delta(E_{\alpha\beta} - \hbar\omega), \tag{30}$$



- **The effect of resonant absorption (and emission) of electromagnetic irradiation at the frequency matching the energy difference in a nuclear system is called Nuclear Magnetic Resonance (NMR).**

1.9. Populations dynamics in two-level system.

- In a two-level system the transition will take place due to the action of external irradiation, but also due to interaction with the environment.



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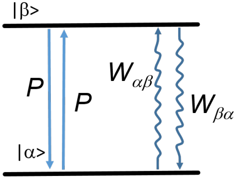

P - the rate of transitions driven by external field, $W_{\alpha\beta}$, $W_{\beta\alpha}$ - rates of spontaneous spin flips due to interaction with environment.

- In thermal equilibrium:

$$N_\alpha^0 W_{\alpha\beta} = N_\beta^0 W_{\beta\alpha}, \text{i.e.} \tag{31}$$

$$\frac{W_{\beta\alpha}}{W_{\alpha\beta}} = exp^{-\frac{\gamma\hbar B_0}{kT}} \approx 1 - \frac{\gamma\beta B_0}{kT} \tag{32}$$

- Equation for populations of levels:

$$\begin{aligned} \frac{dN_\alpha}{dt} &= -N_\alpha(P + W_{\alpha\beta}) + N_\beta(P + W_{\beta\alpha}) \\ \frac{dN_\beta}{dt} &= N_\alpha(P + W_{\alpha\beta}) - N_\beta(P + W_{\beta\alpha}) \end{aligned} \tag{33}$$

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$$\begin{aligned} \frac{dN_\alpha}{dt} &= -N_\alpha(P + W_{\alpha\beta}) + N_\beta(P + W_{\beta\alpha}) \\ \frac{dN_\beta}{dt} &= N_\alpha(P + W_{\alpha\beta}) - N_\beta(P + W_{\beta\alpha}) \end{aligned} \tag{33}$$

- If we introduce the average rate of spontaneous transitions $W = \frac{1}{2}(W_{\alpha\beta} - W_{\beta\alpha})$, then $W_{\alpha\beta} = W(1 + \frac{\gamma\hbar B_0}{2kT})$ and $W_{\beta\alpha} = W(1 - \frac{\gamma\hbar B_0}{2kT})$, the equations can be rewritten:

$$\begin{aligned} \frac{dN_\alpha}{dt} &= (N_\beta - N_\alpha)P + (N_\beta - N_\alpha)W - W\frac{\gamma\beta B_0}{2kT}N \\ \frac{dN_\beta}{dt} &= -(N_\beta - N_\alpha)P - (N_\beta - N_\alpha)W + W\frac{\gamma\beta B_0}{2kT}N \end{aligned} \tag{34}$$

1.9. Populations dynamics in two-level system.

- Denote the population difference as $n = N_\beta - N_\alpha$ and thermal equilibrium population difference $n_0 = N_\beta^0 - N_\alpha^0 \approx N\dfrac{\gamma\hbar B_0}{2kT}$ the equations can be rewritten as:

$$\frac{dn}{dt} = -2nP - 2nW + 2Wn_0, \tag{35}$$

or

$$\frac{dn}{dt} = -2nP - \frac{(n - n_0)}{T_1}, \tag{36}$$

where $T_1 = \dfrac{1}{2W}$ is called spin-lattice relaxation time determines how quickly a spin system reaches a thermal equilibrium with environment.

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- In equilibrium, when $\dfrac{dn}{dt} = 0$:

$$n = \frac{n_0}{1 + 2PT_1} \tag{37}$$

when the power is very large $PT_1 \gg 1$, $n \to 0$, i.e. the system is saturated and no signal can be observed.

Summary of Lecture 2

- Spin $I = \frac{1}{2}$ in a magnetic field. Two-level system.
- System of spins in a magnetic field is capable of absorbing radiation at a resonant frequency.
- Population dynamics in a two-level system. Signal as function of radiation power and saturation.

Suggested reading: Harris 1.5, 1.7, Slichter 1.3
Harris 1.20 - CW NMR spectrometer

- Electrons in atoms in molecules interact with external magnetic field and in turn produce their own magnetic field B_0. The Larmor frequency get shifted in a chemical specific manner - this is known as the chemical shift. The spin Hamiltonian for a nucleus is:

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- Classical illustration of diamagnetic chemical shift:

$$\boldsymbol{\omega} = \frac{e}{2m_e}\mathbf{B_0}$$

$$\mathbf{j} = -e[\boldsymbol{\omega} \times \mathbf{r}]\rho_e = -\frac{e^2}{2m_e}[B_0 \times \mathbf{r}]\rho_e$$

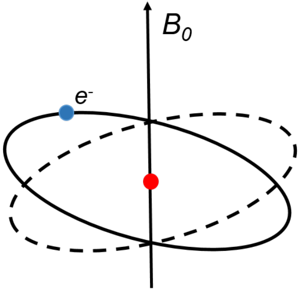
$$d\mathbf{B_i} = \frac{\mu_0}{4\pi r^3}[\mathbf{j} \times \mathbf{r}]dV$$

$$d\mathbf{B_i} = -\frac{\mu_0 e^2}{8\pi m_e r^3}[[\mathbf{B_0} \times \mathbf{r}] \times \mathbf{r}]\rho_e dV$$

$$B_{iz} = -B_0 \frac{\mu_0 e^2}{8\pi m_e}\int \rho_e \frac{x^2+y^2}{r^3}dV$$

Quantum mechanical result:

$$\sigma = -\frac{\mu_0 e^2}{8\pi m_e}\langle\Psi|\frac{x^2+y^2}{r^3}|\Psi\rangle$$



Let's calculate the effect of ring current in cyclic aromatic molecules. Consider benzene molecule:

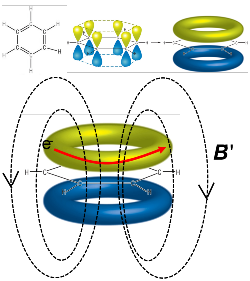


Fig.5: (top) Schematic repsresentation of electron orbitals in a benzene molecule, (bottom) local fields in a benzene molecule produced by electron currents induced by a magnetic field.

- Larmor precession frequency of electrons $\omega_L = \frac{eB_0}{2m_e}$. Current can be calculated as charge $6e$, divided by precession period $\frac{2\pi}{\omega_L}$:

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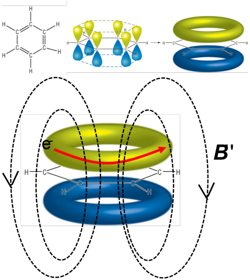

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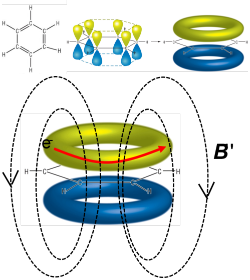

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$$B_i = -\frac{\mu_0}{4\pi}\frac{m}{r^3} = \frac{3\mu_0 e^2}{8\pi}\frac{r^2}{(r+d)^3}B_0 \tag{41}$$

$$\sigma = - - \frac{\mu_0}{4\pi m_e}\frac{m}{r^3} = \frac{3\mu_0 e^2}{8\pi}\frac{r^2}{(r+d)^3} \tag{42}$$

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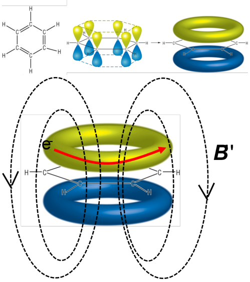

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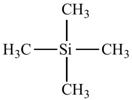
- Given benzene molecule radius $r = 1.4 Å$, CH-bond length $d = 1.1 Å$ we obtain:

$$\sigma \approx -5.3 \cdot 10^{-6}, \sigma_{iso} \approx -1.8 \cdot 10^{-6} \tag{43}$$

2.1. Chemical shifts.

- Chemical shifts are usually measured in ppm's and are referenced with respect to the signals of tetramethylsilane (TMS).



$$\delta = \frac{\nu_{sample} - \nu_{TMS}}{\nu_{TMS}} \times 10^6 \text{ppm} \quad (44)$$

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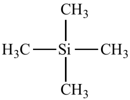

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- In general the ^{1}H chemical shift is greater for nuclei to atoms/bonds that reduce the electron density at the atom.

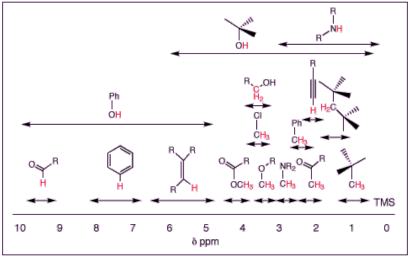

Fig.6: Chemical shifts in various organic molecules Source: `http://orgchem.colorado.edu/Spectroscopy/nmrtheory/protonchemshift.html`

Consider the ^{1}H-spectrum of methyl acetate.

- the TMS appears at 0 ppm

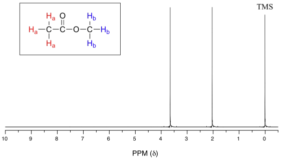

Fig.7: ^{1}H spectrum of methyl acetate. Source: `http://chemwiki.ucdavies.edu/Organic_Chemistry`

Consider the ^{1}H-spectrum of methyl acetate.

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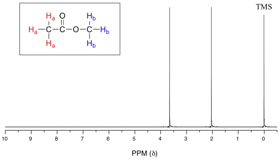
- chemical shift increases from right to left



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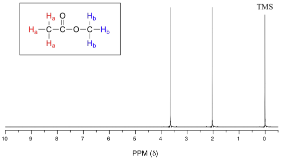

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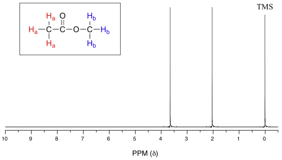

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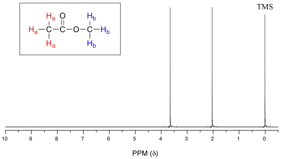

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- the TMS appears at 0 ppm
- chemical shift increases from right to left
- two resonances correpond to protons of the two methyl groups
- the presence of electronegative oxygen atom in methoxy group produces weaker shielding (σ) thus makes bigger chemical shift δ
- three nuclei of methyl groups resonate at the same frequency. Peak heights are the same.

For other nuclei, paramagnetic shifts which arise from mixing of excited state with the ground state dues to the effect of the applicaed field, B_0 on the Hamiltonian can be important, and the range of chemical shifts is usully larger than for ^{1}H nuclei.

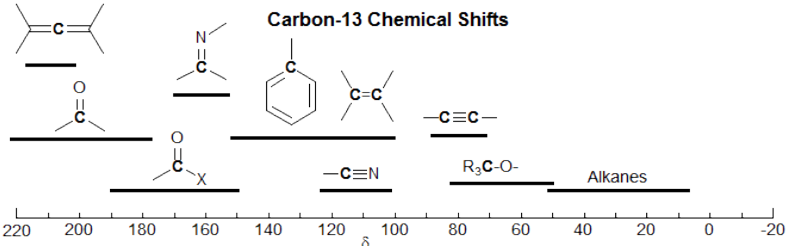

Fig.8: ^{13}C chemical shifts, `https://www.chem.wisc.edu/areas/reich/nmr/`

2.2. J-couplings.

Nuclear spins interact with one another. In solution, one prominent spin-spin interaction is called J-coupling.
This intra-molecular scalar coupling is caused by the combination of two effects: the Pauli principle means that the electons in the bond have opposite spin-state(spin-up and spin-down), while hyperfine couplings (specifically Fermi contact interaction) meanse that it is energetically favourable for each nuclear spin to be anti-parallel to the electron spin.

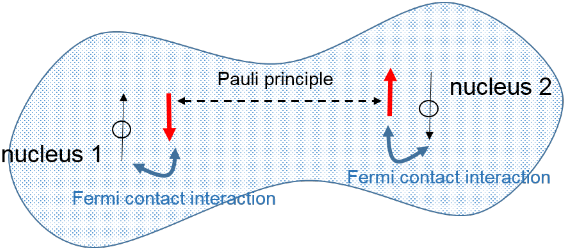

Fig.9: Origin of J-couplings. Low energy configuration in which nuclear spins are antiparallel

2.2. J-couplings.

- Hamiltonian of J-coupling in solution (all anisotropy is averaged):

$$\begin{aligned} \hat{H} &= J\hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 = J(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z}) = \\ &= J\hat{I}_{1z}\hat{I}_{2z} + \frac{J}{2}(\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+}) \end{aligned} \tag{46}$$

  J is usually measured in units of frequency, i.e. Hz.

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  J is usually measured in units of frequency, i.e. Hz.

- In frequency units the full spin Hamiltonian for a system of two nuclei A and B of the same kind would be:

$$\hat{H} = -\nu_0(1-\sigma_A)\hat{I}_{Az} - \nu_0(1-\sigma_B)\hat{I}_{Bz} + J\hat{I}_{Az}\hat{I}_{Bz} + \frac{J}{2}(\hat{I}_{A+}\hat{I}_{B-} + \hat{I}_{A-}\hat{I}_{B+}) \tag{47}$$

- For two coupled spins $\frac{1}{2}$ the Hamiltonian matrix in the basis of functions $|1\rangle = |\alpha_1\alpha_2\rangle, |2\rangle = |\alpha_1\beta_2\rangle, |3\rangle = |\beta_1\alpha_2\rangle, |4\rangle = |\beta_1\beta_2\rangle$ The energy levels of such a system are:

$$H_{ik} = \langle i|\hat{H}|k\rangle = \begin{bmatrix} -\frac{\nu_A+\nu_B}{2}+\frac{J}{4} & 0 & 0 & 0 \\ 0 & -\frac{\nu_A-\nu_B}{2}-\frac{J}{4} & \frac{J}{2} & 0 \\ 0 & \frac{J}{2} & \frac{\nu_A-\nu_B}{2}-\frac{J}{4} & 0 \\ 0 & 0 & 0 & -\frac{\nu_A+\nu_B}{2}+\frac{J}{4} \end{bmatrix} \tag{48}$$

when $|\ \nu_A - \nu_B\ | \gg J$ the off-diagonal terms due to $\hat{I}_{A\pm}\hat{I}_{B\mp}$ can be neglected. That is a called AX system. When off-diagonal terms cannot be neglected, we deal with a so called AB system.

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- Let's consider nuclei of the same type (i.e. both ^{1}H or both ^{13}C). When $\gamma_N\hbar \mid \omega_1 - \omega_2 \mid \ll J$,

2.3. J-couplings in AX system.

Eq.29 is non-zero when corresponding matrix element is not zero. The selection rules for two nuclei then : $\langle i|\hat{I}_{1x} + \hat{I}_{2x}|k\rangle \neq 0$.

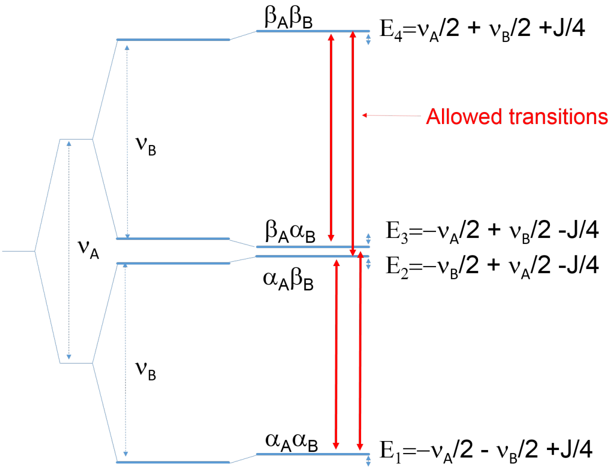


Fig.10: Level diagram for two J-coupled spins in AX system

2.3. J-couplings in AX system.

In a more general case, when $I_A, I_B \neq \frac{1}{2}$, the energy levels follow the following equation:

$$E = -\nu_A m_1 - \nu_0(1 - \sigma_B)m_2 + Jm_1 m_2 \tag{49}$$

The allowed transitions for spin A have the following frequencies:

$$\nu = \nu_A + m_B J, \tag{50}$$

where $m_B = -I_B, -(I_B - 1)...(I_B - 1), I_B$ is the projection of nuclear spin B. The resonance line is therefore being split into several components. Similarly, for spin B:

$$\nu = \nu_B + m_A J, \tag{51}$$

2.3. J-couplings in AX system.

For one coupled nucleus:

$$\nu = \nu_A + m_B J, \tag{52}$$

For two coupled nuclei:

$$\nu = \nu_A + m_B J + m_C J, \tag{53}$$

For three:

$$\nu = \nu_A + m_B J + m_C J + m_D J, \tag{54}$$

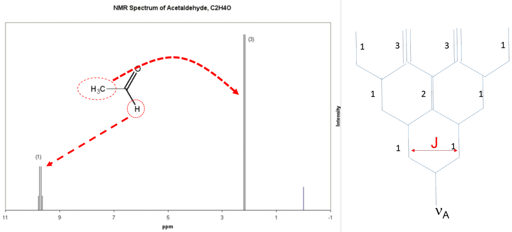
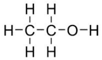


Fig.11: Spectrum of acetaldehyde. Source: `https://chem242.wikispaces.com`

2.3. J-couplings in AX system.

Problem

Draw schematically ^{1}H spectrum of ethyl alcohol? Treat as AX system.



$\delta_{CH3} = 1.22$ ppm, $\delta_{CH2} = 3.68$ ppm, $\delta_{OH} = 2.61$ ppm, consider only $J_{CH2-CH3} = 7.29$ Hz.

2.3. J-couplings in AX system.

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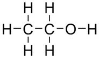

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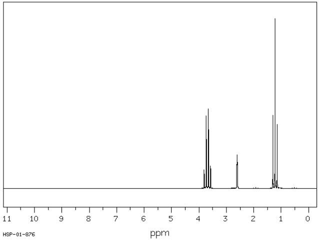


Fig.12: Ethanol spectrum at 90 MHz in $CDCl_3$

2.3. J-couplings in AX system.

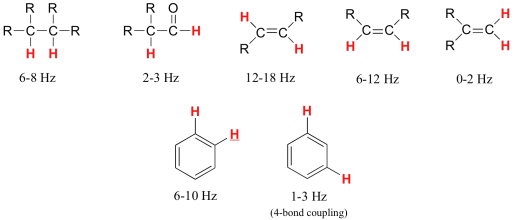
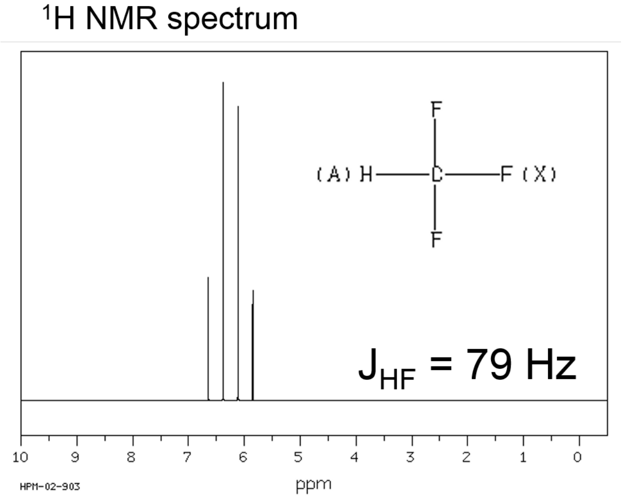


Fig.13: Typical J-couplings `https://chem.libretexts.org/Textbook_Maps/Organic_Chemistry_Textbook_Maps/`

Heteronuclear systems are automatically AX systems, i.e.
$\mid \nu_A - \nu_B \mid \gg J$.
Example: trifluromethane (fluoroform)



2.4. J-coupling in equivalent system.

Are protons in CH3 or CH2 groups coupled to one another?
Yes. But they are equivalent and therefore not observed.

- $$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \qquad (55)$$

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- $$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \tag{55}$$
- Let's rewrite the last term as:

$$\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3 = \frac{1}{2}(\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3)^2 - \frac{1}{2}(\mathbf{I}_1^2 + \mathbf{I}_2^2 + \mathbf{I}_3^2) \tag{56}$$

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Are protons in CH3 or CH2 groups coupled to one another?
Yes. But they are equivalent and therefore not observed.

- $$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \quad (55)$$
- Let's rewrite the last term as:

$$\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3 = \frac{1}{2}(\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3)^2 - \frac{1}{2}(\mathbf{I}_1^2 + \mathbf{I}_2^2 + \mathbf{I}_3^2) \quad (56)$$

- We can introduce new operator: $\mathbf{F} = \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3$. Given that $I_1 = I_2 = I_3 = \frac{1}{2}$ the Hamiltonian can be rewritten using this new operator:

$$\hat{H} = -\nu_0\hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \quad (57)$$

2.4. J-coupling in equivalent system.

Are protons in CH3 or CH2 groups coupled to one another?
Yes. But they are equivalent and therefore not observed.

- $$\hat{H} = -\nu_0(\hat{I}_{1z} + \hat{I}_{2z} + \hat{I}_{3z}) + J(\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_3 + \mathbf{I}_1\mathbf{I}_3) \quad (55)$$
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$$\hat{H} = -\nu_0\hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \quad (57)$$
- Eigenfunctions of this Hamiltonian are functions $|FM_F\rangle$, where $F = \frac{1}{2}$ or $\frac{3}{2}$.

- $$\hat{H} = -\nu_0 \hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \qquad (58)$$

  Selection rules for transitions: $\langle i|\hat{F}_x|k\rangle \neq 0$, since $\hat{F}_x = \frac{\hat{F}_+ + \hat{F}_-}{2}$, the selection rules then are: $\langle i|\hat{F}_\pm|k\rangle \neq 0$
  Since $\hat{F}_\pm = const|FM_F \pm 1\rangle$, the allowed transition does not change the second term in Eq.58.

2.4. J-coupling in equivalent system.

- $$\hat{H} = -\nu_0 \hat{F}_z + J(\mathbf{F}^2 - \frac{9}{4}) \tag{58}$$

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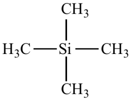
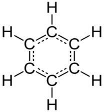
  Since $\hat{F}_\pm = const|FM_F \pm 1\rangle$, the allowed transition does not change the second term in Eq.58.

- Strictly speaking if a molecule contains only nuclei of one type, and no other J-splitting will not be observed. Examples:

  tetramethylsilane (TMS), benzene  

2.5. J-coupling in AB system.

What happens if $\nu_A - \nu_B \gg J$ is no longer true?

- The matrix of spin Hamiltonian is:

$$\begin{bmatrix} -\frac{\nu_A+\nu_B}{2}+\frac{J}{4} & 0 & 0 & 0 \\ 0 & -\frac{\nu_A-\nu_B}{2}-\frac{J}{4} & \frac{J}{2} & 0 \\ 0 & \frac{J}{2} & \frac{\nu_A-\nu_B}{2}-\frac{J}{4} & 0 \\ 0 & 0 & 0 & -\frac{\nu_A+\nu_B}{2}+\frac{J}{4} \end{bmatrix} \tag{59}$$

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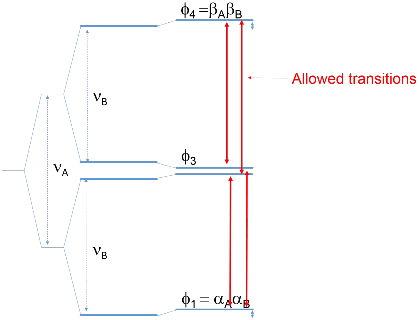
- The general way of solving is finding the eigenvalues and eigenvalues and eigenfunctions of this Hamiltonian.
- the solution can be represented by following replacements:

$$\begin{aligned} &\frac{\nu_A-\nu_B}{2}=\frac{\delta}{2}=C\cos 2\theta \\ &\frac{J}{2}=C\sin 2\theta \\ &C=\frac{1}{2}\sqrt{\delta^2+J^2}, \tan 2\theta=\frac{J}{\delta}, \bar{\nu}=\frac{\nu_A+\nu_B}{2} \end{aligned} \tag{60}$$

2.5. J-coupling in AB system.

In this notation the eigenvalues and eigenfunctions are:

$$
\begin{aligned}
E_1 &= -\bar{\nu} + \frac{J}{4} & \phi_1 &= |\alpha_A\alpha_B\rangle \\
E_2 &= -\frac{J}{4} - C & \phi_2 &= \sin\theta|\alpha_A\beta_B\rangle - \cos\theta|\beta_1\alpha_2\rangle \\
E_3 &= -\frac{J}{4} + C & \phi_2 &= \cos\theta|\alpha_A\beta_B\rangle + \sin\theta|\beta_1\alpha_2\rangle \\
E_4 &= \bar{\nu} + \frac{J}{4} & \phi_4 &= |\beta_A\beta_B\rangle
\end{aligned}
\tag{61}
$$



Problem

Calculate the transition probability between levels 1 and 2?(Hint: use Eq.29)

Fig.14: Level diagram for AB system of J-coupled nuclei.

Problem

Calculate the transition probability between levels 1 and 2?(Hint: use Eq.29)

For transition $1 \leftrightarrow 2$ we have:

$$
\begin{aligned}
&I_{1\leftrightarrow 2} \sim \mid \langle 1|\hat{I}_{Ax} + \hat{I}_{Bx}|2\rangle \mid^2 = \\
&\quad = \langle 1|\frac{\hat{I}_{A+} + \hat{I}_{A-}}{2} + \frac{\hat{I}_{B+} + \hat{I}_{B-}}{2}|2\rangle^2 = \\
&\quad = \left(\langle \alpha_A \alpha_B|\frac{\hat{I}_{A+} + \hat{I}_{A-}}{2} + \frac{\hat{I}_{B+} + \hat{I}_{B-}}{2}|\sin\theta|\alpha_A\beta_B\rangle + \cos\theta|\beta_A\alpha_B\rangle\right)^2 = \\
&\quad = \left(\frac{\cos\theta + \sin\theta}{2}\right)^2 = \frac{1+\sin 2\theta}{4}
\end{aligned}
\tag{62}
$$

For all the transitions we obtain:

Transition	Frequency	Intensity:
$4 \leftrightarrow 2$	$\bar{\nu} + C + \frac{J}{2}$	$\frac{1 - \sin 2\theta}{2}$
$3 \leftrightarrow 1$	$\bar{\nu} + C - \frac{J}{2}$	$\frac{1 + \sin 2\theta}{2}$
$4 \leftrightarrow 3$	$\bar{\nu} - C + \frac{J}{2}$	$\frac{1 + \sin 2\theta}{2}$
$2 \leftrightarrow 1$	$\bar{\nu} - C - \frac{J}{2}$	$\frac{1 - \sin 2\theta}{2}$