<u>NUCLEAR MAGNETIC RESONANCE</u>

Just as IR spectroscopy is the simplest example of transitions being induced by light's oscillating electric field, so NMR is the simplest example of transitions induced by the oscillating magnetic field. Because the strength of matter-magnetic field interactions are typically two orders of magnitude smaller than the corresponding electric field interactions, NMR is a much more delicate probe of molecular structure and properties. The NMR spin Hamiltonians and wavefunctions are particularly simple, and permit us to demonstrate several fundamental principles (about raising and lowering operators, energy levels, transition probabilities, etc.) with a minimal amount of algebra. The principles and procedures are applicable to other areas of spectroscopy -- electronic, vibrational, rotational, etc. – but for these cases the algebra is more extensive.

Nuclear Spins in a Static Magnetic Field

For a single isolated spin in a static magnetic field, the contribution to the energy is:

$$\hat{H}_0 = -\hat{\mathbf{m}} \cdot \mathbf{B}_0 = -\gamma \hat{\mathbf{I}} \cdot \mathbf{B}_0$$

where γ is called the gyromagnetic ratio. If we choose our z axis to point in the direction of the magnetic field then:

$$\hat{H}_0 = -\hat{m}_z B_0 = -\gamma \hat{I}_z B_0$$

If we assume the nuclear spin is ½ (As it is for a proton) then we can easily work out the energy levels of this Hamiltonian:

$$E_\pm = \pm \tfrac{1}{2} \gamma \hbar B_0 \equiv \pm \tfrac{1}{2} \hbar \omega_0$$

where $\omega_0 = \gamma B_0$ is called the nuclear Larmor frequency (rad/sec). Now, nuclei are never isolated in chemistry – they are always surrounded by electrons. As we learned for the hydrogen atom, the electrons near the nucleus shield the outer electrons from the bare electric field produced by the nucleus. Similarly, the electrons shield the nucleus from the bare electric field we apply in the laboratory. More specifically, the electron circulation produces a field, B' opposed to B_0 and of magnitude equal to σB_0 where σ is a constant. Thus, the effective field, B, at the nucleus is
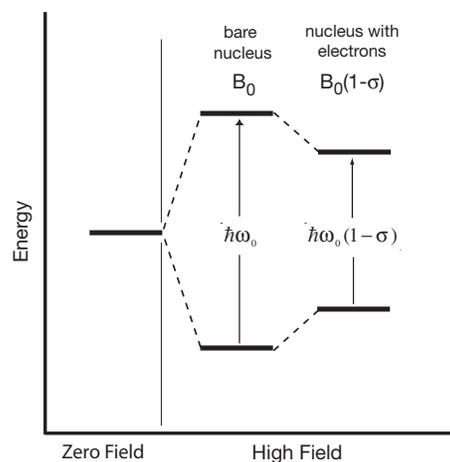
$$B = (1 - \sigma) B_0$$

Note that σ is different for each chemically different nuclear spin – this is the famous *chemical shift* – and permits resolution of lines in NMR spectra corresponding to chemically different sites. The Hamiltonian is modified accordingly

$$\hat{H}_0 = -\hat{m}_z B_0 (1 - \sigma) = -\gamma \hat{I}_z B_0 (1 - \sigma)$$

Thus, instead of "seeing" a magnetic field of magnitude B_0, a proton in a molecule will see a

magnetic field of magnitude $(1-\sigma)B_0$ and the associated Hamiltonian and spin state energies will become:

$$E_\pm = \pm\tfrac{1}{2}\gamma\hbar B_0 (1-\sigma) \equiv \pm\tfrac{1}{2}\hbar\omega_0 (1-\sigma)$$

This is illustrated in the figure above. Note the sign of the Hamiltonian is chosen so that the α state (spin parallel to B_0) is lower in energy than the β state (spin antiparallel to B_0).

Now, in the simplest NMR experiment, we probe this system with an oscillating magnetic field perpendicular to the static field. By convention, we take this field to be along the x axis:

$$\hat{H}_1(t) = -\hat{\mathbf{m}}\cdot\mathbf{B}_1(t) = -\gamma\hat{\mathbf{I}}\cdot\mathbf{B}_1(t) = -\gamma\,\hat{I}_x B_x \cos(\omega t)$$

We use Fermi's Golden Rule to describe the spectrum of the spin in the oscillating field. The selection rule is:

$$\left|V_{fi}\right|^2 = \left|\int \phi_f{}^* \mathbf{m}\cdot\mathbf{B}_1 \phi_i d\tau\right|^2 = \left|\gamma\, B_x \cdot \int \phi_f{}^* \hat{I}_x \phi_i d\tau\right|^2$$

Now, we recall that $\hat{I}_x$ can be written in terms of the raising and lowering operators for angular momentum:

$$\hat{I}_x \propto \left(\hat{I}_+ + \hat{I}_-\right)$$

So that:

$$\left|V_{fi}\right|^2 \propto \left|\gamma\, B_x \cdot \int \phi_f{}^* \left(\hat{I}_+ + \hat{I}_-\right)\phi_i d\tau\right|^2$$

We immediately see that the integral is non-zero only if the initial and final spin states differ by ± 1 quantum of angular momentum (i.e. $\Delta M = \pm 1$) , because the operator must either raise or lower the eigenvalue of $\hat{I}_z$. Thus, there are two possible transitions: $\alpha\rightarrow\beta$ and $\beta\rightarrow\alpha$. Futher, the energy conservation rule tells us that these transitions will only occur when the photon energy matches the energy gap between the two states. As a result, we can immediately draw the spectrum of a single shielded spin:
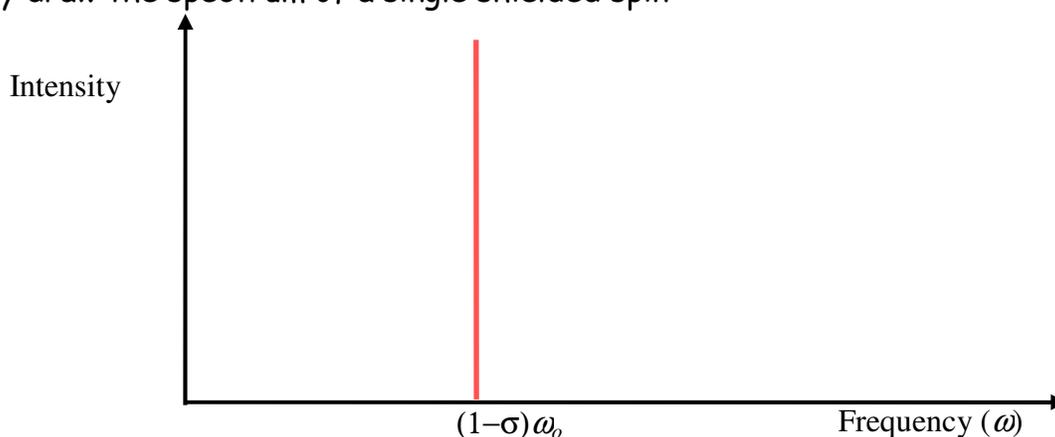

This is perhaps not all that shocking: there is only one transition here, and so we might have guessed that the spectrum would involve the frequency of that transition. However, we note two generalizations of this result. First, we note that if we had chosen to apply the oscillating field parallel to the static field, we would not have generated any transitions; we

only changed the spin state because we could decompose the x-oscillating field into raising and lowering operators. If the field was z-oscillating, then we would have had

$$\left|V_{fi}\right|^2 \propto \left|\gamma B_x \cdot \int \phi_f^* \hat{I}_z \phi_i d\tau\right|^2$$

which is only non-zero for the trivial $\alpha \to \alpha$ and $\beta \to \beta$ transitions. Second, we note that if the spin was bigger than $\frac{1}{2}$ (e.g. a spin-3/2 nucleus) then our selection rule above would be precisely the same. Thus, we would have allowed transitions $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$, $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ and $+\frac{1}{2} \leftrightarrow +\frac{3}{2}$ and all of these transitions would occur at the same frequency. Thus, spin-3/2 transitions like $-\frac{3}{2} \leftrightarrow +\frac{1}{2}$ or $-\frac{3}{2} \leftrightarrow +\frac{3}{2}$ are strictly forbidden.

Now, as noted above, depending on their environment, different protons will be shielded differently, resulting in a spectrum that will look qualitatively like:
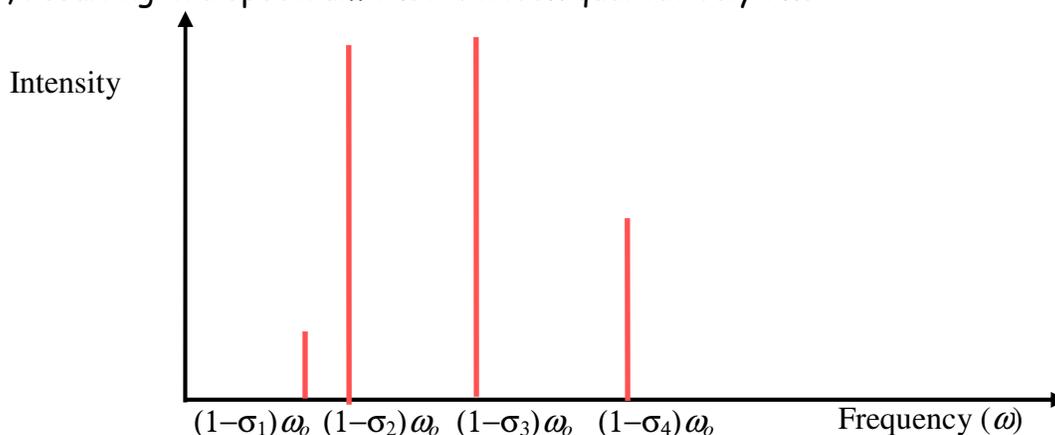
We note that the transition moment above is independent of the chemical environment: it does not depend on shielding or any other property of the molecule. Thus, the area under an NMR peak is strictly proportional to the number of spins that have transitions at that frequency. This stands in contrast to IR spectroscopy, where the intensity of each oscillator depended on the character of the oscillator, the initial state ….

Two Spins – J Couplings
Now, we are not usually interested in two isolated spins. For two <u>uncoupled spins</u> with different chemical shifts ($\sigma_1 \neq \sigma_2$) in an external field we obtain a Hamiltonian of the form:

$$\hat{H}_0 = -\gamma \hat{I}_{1z} B_0 (1 - \sigma_1) - \gamma \hat{I}_{2z} B_0 (1 - \sigma_2)$$

Because this Hamiltonian is separable, we can immediately work out the energies:

$$E_{\downarrow\downarrow} = E_{1\downarrow} + E_{2\downarrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1) + (1-\sigma_2)\right]$$

$$E_{\downarrow\uparrow} = E_{1\downarrow} + E_{2\uparrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1) - (1-\sigma_2)\right]$$

$$E_{\uparrow\downarrow} = E_{1\uparrow} + E_{2\downarrow} = -\frac{\omega_o}{2}\left[(1-\sigma_1) - (1-\sigma_2)\right]$$
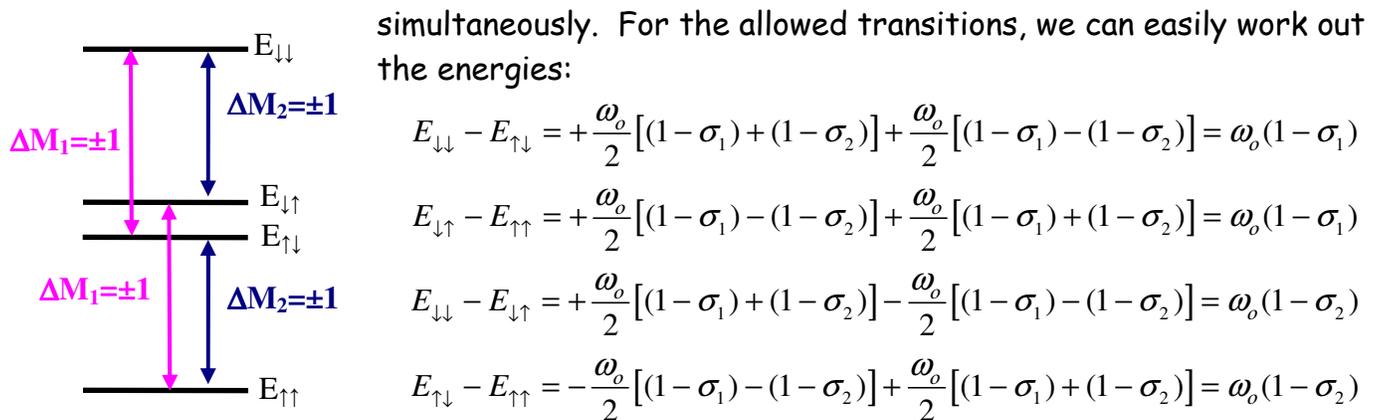
$$E_{\uparrow\uparrow} = E_{1\uparrow} + E_{2\uparrow} = -\frac{\omega_o}{2}\left[(1-\sigma_1) + (1-\sigma_2)\right]$$

where we have assumed for simplicity that $\sigma_1 < \sigma_2$ so that $E_{\downarrow\uparrow} > E_{\uparrow\downarrow}$. Now, the selection rule is the of the same form as for a single spin, but I_x decomposes into a sum of I_x for spin 1 and an I_x for spin 2:

$$\left|V_{fi}\right|^2 = \left|\gamma\, B_x \bullet \int \phi_f^* \hat{I}_x \phi_i d\tau\right|^2 = \left|\gamma\, B_x \bullet \int \phi_f^* \left(\hat{I}_{1x} + \hat{I}_{2x}\right) \phi_i d\tau\right|^2$$

$$\propto \left|\int \phi_f^* \left(\hat{I}_{1+} + \hat{I}_{1-} + \hat{I}_{2+} + \hat{I}_{2-}\right) \phi_i d\tau\right|^2$$

The remaining integral is only nonzero if $\Delta M_1 = \pm 1$ **_or_** $\Delta M_2 = \pm 1$, because the operators must raise or lower the spin state of **either** spin 1 **or** spin 2 (but not both). If we wanted to change both spins, we would need an operator like $\hat{I}_{1+}\hat{I}_{2-}$, which would allow us to raise 1 while also lowering 2. Since we do not have any of these cross terms, we conclude only one or the other spin can flip in an allowed transition – any two-spin transitions are forbidden.

Combining these results for two uncoupled spins, we obtain the picture at left. We note that the $\uparrow\uparrow\leftrightarrow\downarrow\downarrow$ and $\downarrow\uparrow\leftrightarrow\uparrow\downarrow$ transitions are forbidden, since they require flipping both spins simultaneously. For the allowed transitions, we can easily work out the energies:

$$E_{\downarrow\downarrow} - E_{\uparrow\downarrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1)+(1-\sigma_2)\right] + \frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)\right] = \omega_o(1-\sigma_1)$$

$$E_{\downarrow\uparrow} - E_{\uparrow\uparrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)\right] + \frac{\omega_o}{2}\left[(1-\sigma_1)+(1-\sigma_2)\right] = \omega_o(1-\sigma_1)$$

$$E_{\downarrow\downarrow} - E_{\downarrow\uparrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1)+(1-\sigma_2)\right] - \frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)\right] = \omega_o(1-\sigma_2)$$

$$E_{\uparrow\downarrow} - E_{\uparrow\uparrow} = -\frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)\right] + \frac{\omega_o}{2}\left[(1-\sigma_1)+(1-\sigma_2)\right] = \omega_o(1-\sigma_2)$$

So we have only two transition energies, corresponding to each of the isolated transitions, just as predicted above:
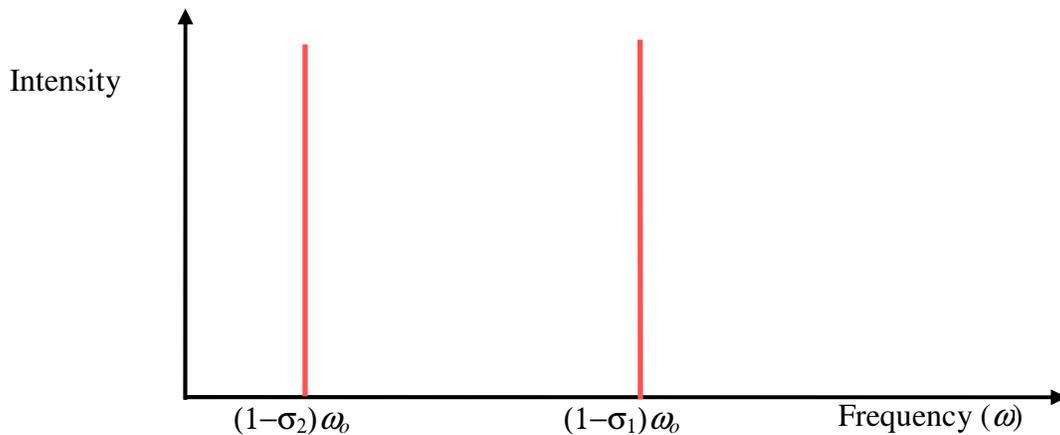
Where we note that there are actually two degenerate transitions contributing to each line.

We now permit the two spins to be coupled to one another in a simple way. We include a J-coupling of the spins: $\dfrac{J}{\hbar^2}\hat{I}_{1z}\hat{I}_{2z}$, where the factors of $\hbar$ are included so that J has units of energy. Thus, the Hamiltonian assumes the form

$$\hat{H}_0 = -\gamma\hat{I}_{1z}B_0\left(1-\sigma_1\right) - \gamma\hat{I}_{2z}B_0\left(1-\sigma_2\right) + \frac{J}{\hbar^2}\hat{I}_{1z}\hat{I}_{2z}$$

Now, we can work out the eigenvalues of this new Hamiltonian quite easily because we know the eigenvalues of $\hat{I}_{1z}$ and $\hat{I}_{2z}$. For example, for the ↓↓ state:

$$\hat{H}_0\phi_{\downarrow\downarrow} = \left(-\gamma\hat{I}_{1z}B_0\left(1-\sigma_1\right) - \gamma\hat{I}_{2z}B_0\left(1-\sigma_2\right) + \frac{J}{\hbar^2}\hat{I}_{1z}\hat{I}_{2z}\right)\phi_{\downarrow\downarrow}$$

$$= \left(E_{1\downarrow} + E_{2\downarrow} + \frac{J}{\hbar^2}\left(\frac{-\hbar}{2}\right)\left(\frac{-\hbar}{2}\right)\right)\phi_{\downarrow\downarrow}$$

$$= \left(E_{1\downarrow} + E_{2\downarrow} + \frac{J}{4}\right)\phi_{\downarrow\downarrow}$$

Similar algebra for the other states gives:

$$\hat{H}_0\phi_{\uparrow\downarrow} = \left(E_{1\uparrow} + E_{2\downarrow} + \frac{J}{\hbar^2}\left(\frac{\hbar}{2}\right)\left(\frac{-\hbar}{2}\right)\right)\phi_{\uparrow\downarrow} = \left(E_{1\uparrow} + E_{1\downarrow} - \frac{J}{4}\right)\phi_{\uparrow\downarrow}$$

$$\hat{H}_0\phi_{\downarrow\uparrow} = \left(E_{1\downarrow} + E_{2\uparrow} + \frac{J}{\hbar^2}\left(\frac{-\hbar}{2}\right)\left(\frac{\hbar}{2}\right)\right)\phi_{\downarrow\uparrow} = \left(E_{1\downarrow} + E_{2\uparrow} - \frac{J}{4}\right)\phi_{\downarrow\uparrow}$$

$$\hat{H}_0\phi_{\uparrow\uparrow} = \left(E_{1\uparrow} + E_{2\uparrow} + \frac{J}{\hbar^2}\left(\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right)\right)\phi_{\uparrow\uparrow} = \left(E_{1\uparrow} + E_{1\downarrow} + \frac{J}{4}\right)\phi_{\uparrow\uparrow}$$

Thus, in the presence of the coupling, our energy diagram changes:

Uncoupled   J Coupling
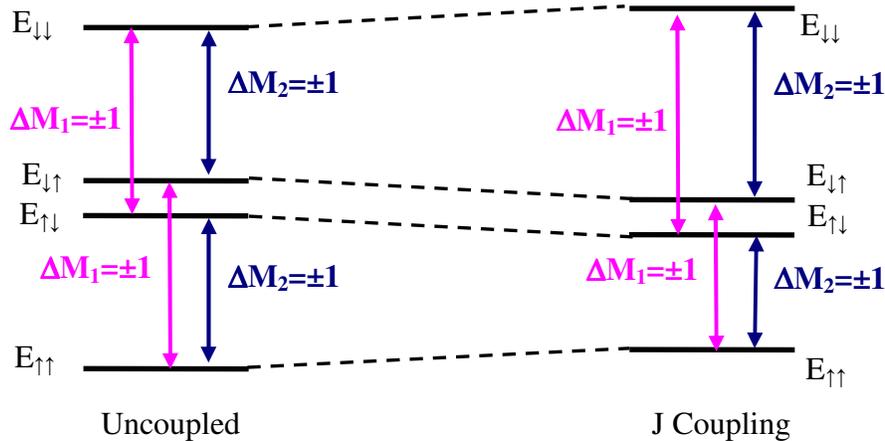
Where we have noted that states where the spins are parallel shift upward in energy and those where the spins are antiparallel shift down, and we have exaggerated the magnitude of the shift for visual effect. Note that the selection rules do not change, because **the states have not changed** – only the energies are different with the coupling on. The energies of the allowed transitions are:
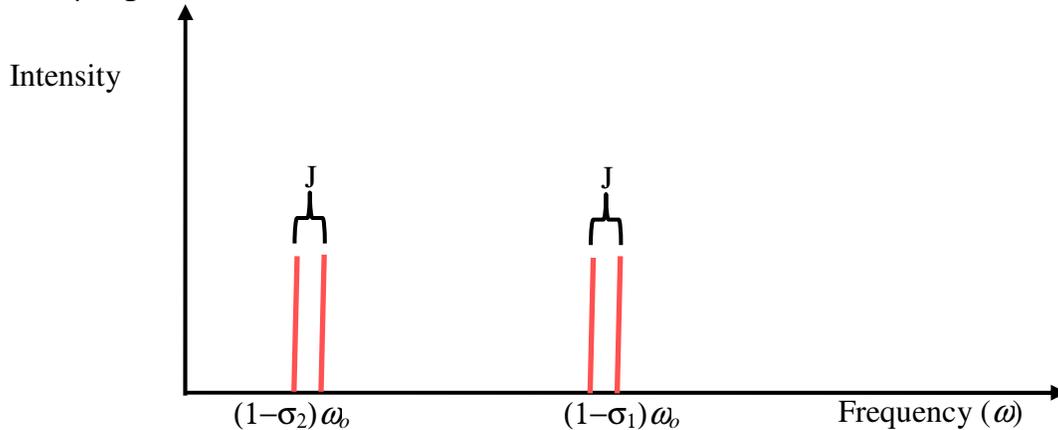
$$E_{\downarrow\downarrow} - E_{\uparrow\downarrow} = +\frac{\omega_o}{2}\left[\left(1-\sigma_1\right) + \left(1-\sigma_2\right) + \frac{J}{4}\right] - \frac{\omega_o}{2}\left[-\left(1-\sigma_1\right) + \left(1-\sigma_2\right) - \frac{J}{4}\right] = \omega_o\left(1-\sigma_1\right) + \frac{J}{2}$$

$$E_{\downarrow\uparrow} - E_{\uparrow\uparrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)-\frac{J}{4}\right]-\frac{\omega_o}{2}\left[-(1-\sigma_1)-(1-\sigma_2)+\frac{J}{4}\right]=\omega_o(1-\sigma_1)-\frac{J}{2}$$

$$E_{\downarrow\downarrow} - E_{\downarrow\uparrow} = +\frac{\omega_o}{2}\left[(1-\sigma_1)+(1-\sigma_2)+\frac{J}{4}\right]-\frac{\omega_o}{2}\left[(1-\sigma_1)-(1-\sigma_2)-\frac{J}{4}\right]=\omega_o(1-\sigma_2)+\frac{J}{2}$$

$$E_{\uparrow\downarrow} - E_{\uparrow\uparrow} = \frac{\omega_o}{2}\left[-(1-\sigma_1)+(1-\sigma_2)-\frac{J}{4}\right]-\frac{\omega_o}{2}\left[-(1-\sigma_1)-(1-\sigma_2)+\frac{J}{4}\right]=\omega_o(1-\sigma_2)-\frac{J}{2}$$

Thus, whereas we had two doubly degenerate transitions in the absence of coupling, in the presence of coupling we have four distinct transitions:

where here we have noted the physical fact that J is typically much smaller than the difference in chemical shielding σ between distinct protons. Thus, we see that the splitting of NMR peaks is mediated by the coupling between the nuclear spins. This coupling is typically mediated via the electrons – nucleus 1 pushes on the electrons, which are delocalized and in turn push on nucleus 2. While one can routinely compute these couplings via DFT or HF, it is much more common to use empirical rules to determine which protons will be coupled and how large we expect the coupling to be. We should note that the magnitude of the J-splitting is independent of the magnetic field strength. Meanwhile, the Larmor frequency increases with increasing B_0. Thus, in a strong enough magnet, the peaks with shielding near σ_1 will be very far from those with shielding σ_2.

Spin Dynamics and Pulsed NMR

One of the extremely appealing aspects of NMR is we can exactly work out virtually any property we're interested in knowing. In particular, we can get a picture of the **dynamics** of the spin in an external magnetic field. This gives us a qualitative picture of what we are doing when we take an NMR spectrum and also serves as the basis for modern pulsed NMR experiments. Consider an arbitrary initial state written as a linear combination of the two spin states:

$$\psi(t) = c_\alpha(t)\psi_\alpha + c_\beta(t)\psi_\beta$$

where we have noted that the time dependence of the state comes through the time dependence of the coefficients. We can write this in matrix mechanics:

$$\vec{\psi}(t) = \begin{pmatrix} c_\alpha(t) \\ c_\beta(t) \end{pmatrix}$$

We can also write the time-dependent Schrödinger equation in Matrix mechanics:

$$i\hbar\dot{\psi}(t) = \hat{H}\psi(t) \quad \Rightarrow \quad i\hbar\begin{pmatrix} \dot{c}_\alpha(t) \\ \dot{c}_\beta(t) \end{pmatrix} = \begin{pmatrix} H_{\alpha\alpha} & H_{\alpha\beta} \\ H_{\beta\alpha} & H_{\beta\beta} \end{pmatrix}\begin{pmatrix} c_\alpha(t) \\ c_\beta(t) \end{pmatrix}$$

Now, for a spin in a static field, we know the Hamiltonian

$$\hat{H} = -\omega_0(1-\sigma)\hat{I}_z \equiv -\tilde{\omega}_0\hat{I}_z \quad \Rightarrow \quad \mathbf{H} = -\tilde{\omega}_0\mathbf{I_z} = \begin{pmatrix} \dfrac{-\hbar\tilde{\omega}_0}{2} & 0 \\ 0 & \dfrac{\hbar\tilde{\omega}_0}{2} \end{pmatrix}$$

Thus, the TDSE becomes:

$$i\hbar\begin{pmatrix} \dot{c}_\alpha(t) \\ \dot{c}_\beta(t) \end{pmatrix} = \begin{pmatrix} \dfrac{-\hbar\tilde{\omega}_0}{2} & 0 \\ 0 & \dfrac{-\hbar\tilde{\omega}_0}{2} \end{pmatrix}\begin{pmatrix} c_\alpha(t) \\ c_\beta(t) \end{pmatrix}$$

Which reduces to two independent differential equations for the coefficients:

$$i\hbar\dot{c}_\alpha(t) = \frac{-\hbar\tilde{\omega}_0}{2}c_\alpha(t) \qquad i\hbar\dot{c}_\beta(t) = \frac{+\hbar\tilde{\omega}_0}{2}c_\beta(t)$$

These equations can easily be integrated to yield:

$$c_\alpha(t) = e^{\frac{+i\tilde{\omega}_0 t}{2}}c_\alpha(0) \qquad c_\beta(t) = e^{\frac{-i\tilde{\omega}_0 t}{2}}c_\beta(0)$$

where we will assume for simplicity that the initial values, $c_\alpha(0), c_\beta(0)$ are real. Thus, the magnitude of each coefficient is constant with time; we only acquire a phase factor for each coefficient. However, these coefficients completely describe the time evolution of an arbitrary spin state in the static magnetic field.

Now that we have solved for the coefficients of the time dependent wavefunction, let's look at some interesting properties of the system. First, let's compute the z-component of the spin:

$$\langle\hat{I}_z\rangle(t) = \begin{pmatrix} c_\alpha(t)* & c_\beta(t)* \end{pmatrix}\begin{pmatrix} \dfrac{\hbar}{2} & 0 \\ 0 & -\dfrac{\hbar}{2} \end{pmatrix}\begin{pmatrix} c_\alpha(t) \\ c_\beta(t) \end{pmatrix} = \frac{\hbar}{2}\Big[\big|c_\alpha(t)\big|^2 - \big|c_\beta(t)\big|^2\Big] = \frac{\hbar}{2}\Big[\big|c_\alpha(0)\big|^2 - \big|c_\beta(0)\big|^2\Big]$$

Thus, **the z-component of the spin does not change with time**! This is perhaps a bit surprising. We continue to compute the x and y components:

$$\langle\hat{I}_x\rangle(t) = \begin{pmatrix} c_\alpha(t)* & c_\beta(t)* \end{pmatrix}\begin{pmatrix} 0 & \dfrac{\hbar}{2} \\ \dfrac{\hbar}{2} & 0 \end{pmatrix}\begin{pmatrix} c_\alpha(t) \\ c_\beta(t) \end{pmatrix} = \frac{\hbar}{2}\Big[c_\alpha(t)* c_\beta(t) + c_\beta(t)* c_\alpha(t)\Big]$$

$$= \frac{\hbar}{2}c_\alpha(0)c_\beta(0)\Big[e^{-i\tilde{\omega}_0 t} + e^{+i\tilde{\omega}_0 t}\Big] = \hbar c_\alpha(0)c_\beta(0)\cos\tilde{\omega}_0 t$$

$$\left\langle \hat{I}_y \right\rangle (t) = \begin{pmatrix} c_\alpha (t)* & c_\beta (t)* \end{pmatrix} \begin{pmatrix} 0 & \dfrac{-i\hbar}{2} \\ \dfrac{i\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} c_\alpha (t) \\ c_\beta (t) \end{pmatrix} = \dfrac{-i\hbar}{2} \left[c_\alpha (t)* c_\beta (t) - c_\beta (t)* c_\alpha (t) \right]$$

$$= \dfrac{-i\hbar}{2} c_\alpha (0) c_\beta (0) \left[e^{-i\tilde{\omega}_0 t} - e^{+i\tilde{\omega}_0 t} \right] = -\hbar c_\alpha (0) c_\beta (0) \sin \tilde{\omega}_0 t$$

Thus, the x and y components oscillate with time at the shielded Larmor frequency $\tilde{\omega}_0$. It is convenient to define a magnetization vector that contains these three expectation values:

$$\vec{M} (t) \equiv \left(\left\langle \hat{I}_x \right\rangle (t) \quad \left\langle \hat{I}_y \right\rangle (t) \quad \left\langle \hat{I}_z \right\rangle (t) \right)$$

It is fairly easy to see that the magnetization is precessing about the magnetic field: the projection onto the magnetic field axis is constant, while the perpendicular motion is tracing out a circular path. This is precisely the behavior one would expect from a classical magnetic moment in a magnetic field. In this case, the magnetic field would exert a torque on the magnetic moment according to:

$$\dfrac{d\vec{M} (t)}{dt} = \vec{M} (t) \times \gamma \vec{B}^{eff}$$

where we note that the magnetic moment feels the shielded magnetic field B^{eff}. This gives us three differential equations for the components of the magnetization, called **Bloch Equations**:

$$\dfrac{dM_x (t)}{dt} = \gamma \left[M_y (t) B_z^{eff} - M_z (t) B_y^{eff} \right] = \gamma M_y (t) B_z^{eff}$$

$$\dfrac{dM_y (t)}{dt} = -\gamma \left[M_x (t) B_z^{eff} - M_z (t) B_x^{eff} \right] = -\gamma M_x (t) B_z^{eff}$$

$$\dfrac{dM_z (t)}{dt} = \gamma \left[M_x (t) B_y^{eff} - M_y (t) B_x^{eff} \right] = 0$$

Where we have noted that only the z-component of the magnetic field is non-zero. Further, it is easy to see by substitution that our quantum mechanical predictions for $\left\langle \hat{I}_x \right\rangle (t)$ and $\left\langle \hat{I}_y \right\rangle (t)$ satisfy the equations above for $M_x (t)$ and $M_y (t)$, respectively (try it and see). Thus, we find that **the quantum evolution of the average spin exactly follows the classical equations of motion**! We find comfort in this conclusion, because it is usually much easier to think in terms of classical properties whenever possible, giving us a very nice semiclassical way of interpreting NMR.

This rather surprising result turns out to be true for a single spin evolving in an arbitrary time dependent magnetic field $B^{eff}(t)$. To prove this, we have to use Ehrenfest's theorem, which states that for an arbitrary operator O, the time dependent average value of O satisfies

$$\dfrac{d}{dt} \left\langle \hat{O} \right\rangle (t) = \dfrac{i}{\hbar} \left\langle \left[\hat{H}, \hat{O} \right] \right\rangle (t)$$

We proved a shortened version of this on one of the Problem Sets. Applying Ehrenfests theorem to the three operators $\hat{I}_x, \hat{I}_y, \hat{I}_z$ in an arbitrary magnetic field $B^{eff}(t)$ gives equations of motion that are exactly the same as the classical equations for $\vec{M}(t)$. Thus, one can prove quite rigorously that the classical picture is exactly right for describing spin dynamics in a magnetic field.

What does this gain us? Well, with this result in hand it is relatively easy to derive the correct differential equations for our favorite time dependent magnetic field:

$$\vec{B}^{eff}(t) = -B_z^{eff} - B_x \cos(\omega t)$$

This is the magnetic field we apply in an NMR experiment and being able to visualize the dynamics will help us understand how the experiment works. It is relatively straightforward to work out the associated Bloch Equations for this magnetic field. They are:

$$\frac{dM_x(t)}{dt} = \gamma M_y(t) B_z^{eff}$$

$$\frac{dM_y(t)}{dt} = -\gamma \left[M_x(t) B_z^{eff} + M_z(t) B_x \cos(\omega t) \right]$$

$$\frac{dM_z(t)}{dt} = -\gamma M_y(t) B_x \cos(\omega t)$$

These equations can actually be solved analytically to obtain the magnetization as a function of time. From these equations we obtain the picture below:

$$\omega \gg \omega_0 \qquad\qquad \omega = \omega_0 \qquad\qquad \omega \ll \omega_0$$
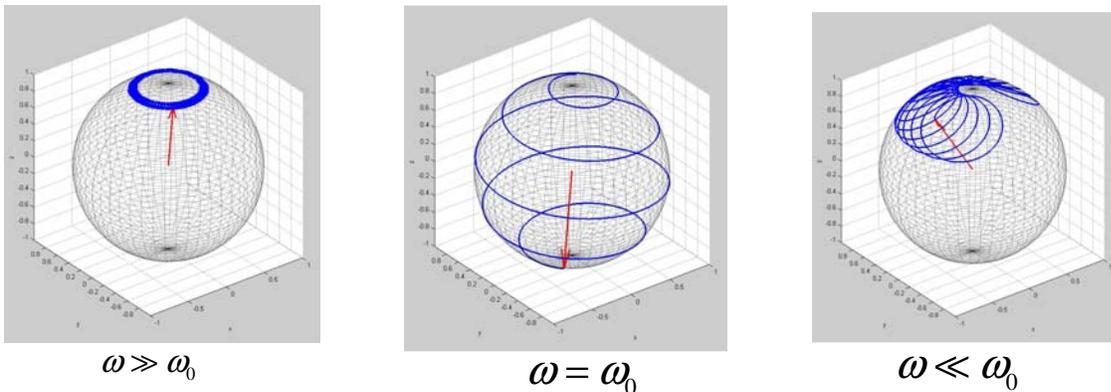
Here, we are plotting the magnetization as a function of time for various choices of the frequency of the oscillating magnetic field component. If our field oscillates too quickly (first case) then the magnetization just sees the average field and noting interesting happens – we just get precession about the average field. If the oscillating field is too slow, the magnetization oscillates around the instantaneous field and we get a sort of hula-hoop motion of the magnetization. However, if we hit the frequency just right (middle) we can get the magnetization to invert – to go from "up" to "down". Thus, we see that the absorption condition in NMR is associated with flipping the magnetization of the system.

Now, we note that at resonance, with the field on continuously, the spin will actually flip from "up" to "down" and back to "up" and back to "down"… as a function of time. It is this

oscillation that shows up in our NMR spectrum. However, it is possible to turn the oscillating field on and off as a function of time. Thus, for example, if we kept the field on for exactly π/ω_0 then the system would only have time to flip one time – all the up spins would be converted to down and vice versa. Such a pulsed magnetic field is called an inversion pulse, for obvious reasons. Meanwhile, if we kept the field on for exactly $\pi/2\omega_0$ we could drive all the magnetization into the x-y plane. This is called a $\pi/2$ pulse. Further, we note these pulses only work if we are on resonance with a particular proton's Larmor frequency; from the above figure it is clear that if we are off resonance, we can't get the spins to flip. Thus, one can imagine fairly complex sequences of inversion pulses and $\pi/2$ pulses applied at various frequencies being used to isolate different couplings within a complicated molecule (like a protein). Thus, it should not be surprising that cutting edge NMR experiments are all time-resolved in order to extract the maximum information from the molecule.