Module I, Lecture 12: Rotating Frame Approximation

Interaction representation

Because Zeeman interactions commonly encountered in magnetic resonance are fairly large (from MHz to THz in practically encountered magnets), it is usually inconvenient to calculate the spin system trajectory $G(\hat{\rho}_0)$ from a given initial state $\hat{\rho}_0$ using the full Hamiltonian superoperator $\hat{\hat{H}}$:

$$G(\hat{\rho}_0)=\left\{e^{-i\hat{\hat{H}}t}\hat{\rho}_0,\ t\in[0,\infty)\right\}\quad\Rightarrow\quad G(\hat{\rho}_0)=\left\{\hat{\rho}_0,\hat{\hat{P}}\hat{\rho}_0,\hat{\hat{P}}^2\hat{\rho}_0,...\right\}\qquad \hat{\hat{P}}=e^{-i\hat{\hat{H}}\Delta t},\ \Delta t\approx\|\hat{\hat{H}}\|^{-1}$$

because the time step Δt required to sample the system trajectory accurately is extremely small (microseconds to picoseconds) on the time scale of the simulation (seconds). The following transformation (called *interaction representation transformation* or *rotating frame transformation*) is often applied to get rid of the large Zeeman terms in Liouville space:

$$\frac{d}{dt}\hat{\rho}(t)=-i\left(\hat{\hat{H}}_0+\hat{\hat{H}}_1\right)\hat{\rho}(t)\qquad \hat{\hat{H}}=\mathrm{ad}\hat{H}=[\hat{H},\ ]$$

$$\hat{\sigma}(t)=e^{i\hat{\hat{H}}_0t}\hat{\rho}(t)\qquad \hat{\hat{H}}_1^{\mathrm{R}}(t)=e^{i\hat{\hat{H}}_0t}\hat{\hat{H}}_1e^{-i\hat{\hat{H}}_0t}\quad\Rightarrow\quad\frac{d}{dt}\hat{\sigma}(t)=-i\hat{\hat{H}}_1^{\mathrm{R}}(t)\hat{\sigma}(t)$$

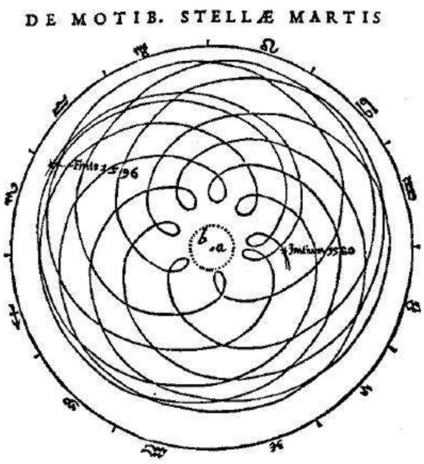
This result is easy to verify by explicit substitution and simplification. Similarly, in Hilbert space:

$$\frac{d}{dt}\hat{\rho}(t)=-i\left[\hat{H}_0+\hat{H}_1,\hat{\rho}(t)\right]$$

$$\hat{\sigma}(t)=e^{i\hat{H}_0t}\hat{\rho}(t)e^{-i\hat{H}_0t}\qquad \hat{H}_1^{\mathrm{R}}(t)=e^{i\hat{H}_0t}\hat{H}_1e^{-i\hat{H}_0t}\quad\Rightarrow\quad\frac{d}{dt}\hat{\sigma}(t)=-i\left[\hat{H}_1^{\mathrm{R}}(t),\hat{\sigma}(t)\right]$$

with the result that the "large and simple" term $\hat{H}_0$ disappears from the equation and the "small and complicated" term $\hat{H}_1$ acquires time dependence because it is now wrapped in $\hat{H}_0$ propagators.

Because $SO(n)$ is a subgroup of $SU(n)$, we could say that the transformation above is a (perhaps complicated) rotation. In the case where $\hat{H}_0$ is Zeeman interaction of one spin, the interaction representation transformation does actually amount to a simple rotation in the physical sense: $\exp\left(-i\hat{L}_Z\varphi\right)$ rotates the system by an angle φ in the XY plane, hence the "rotating frame" term. The case where interaction representation is invoked with respect to all Zeeman interactions in the system is not easy to visualize and is best approached as a formal unitary transformation.



The trajectory of Mars in the geocentric reference frame, including several periods of apparent retrograde motion (Johannes Kepler, "Astronomia Nova", 1609) – an example of an unfortunate choice of interaction representation.

Secular parts of spin interactions

Because of its ubiquity, the case of interaction representation transformation with respect to Zeeman Hamiltonian deserves special attention. Some types of interactions commute with $\hat{L}_Z$, and therefore $\exp\left(-i\hat{L}_Zt\right)$, and are unaffected by the interaction representation transformation:

$$[\hat{L}_Z,\hat{L}_Z\hat{S}_Z]=[\hat{S}_Z,\hat{L}_Z\hat{S}_Z]=0,\qquad [\hat{L}_Z+\hat{S}_Z,\hat{L}_X\hat{S}_X+\hat{L}_Y\hat{S}_Y+\hat{L}_Z\hat{S}_Z]=0$$

Note that the scalar coupling operator $\hat{L}_X\hat{S}_X+\hat{L}_Y\hat{S}_Y+\hat{L}_Z\hat{S}_Z$ does not commute with $\hat{L}_Z$ and $\hat{S}_Z$ individually. Irreducible spherical tensor basis is particularly convenient here – it is ordered with respect to this commutation property:

$$[\hat{L}_Z,\hat{T}_{lm}(L)]=\hat{\hat{L}}_Z\hat{T}_{lm}(L)=m\hat{T}_{lm}(L),\quad [\hat{L}_Z+\hat{S}_Z,\hat{T}_{lm}(L,S)]=\left(\hat{\hat{L}}_Z+\hat{\hat{S}}_Z\right)\hat{T}_{lm}(L,S)=m\hat{T}_{lm}(L,S)$$

This allows us to evaluate the rotating frame expressions:

$$e^{i\omega\hat{L}_Z t}\hat{T}_{lm}(L)e^{-i\omega\hat{L}_Z t}=e^{i\omega\hat{\hat{L}}_Z t}\hat{T}_{lm}(L)=$$
$$=\sum_{n=0}^{\infty}\frac{(i\omega t)^n}{n!}\hat{\hat{L}}_Z^n\hat{T}_{lm}(L)=\sum_{n=0}^{\infty}\frac{(im\omega t)^n}{n!}\hat{T}_{lm}(L)=e^{im\omega t}\hat{T}_{lm}(L)$$

Similarly, for two-spin irreducible spherical tensor operators:

$$e^{i\omega\left(\hat{L}_Z+\hat{S}_Z\right)t}\hat{T}_{lm}(L,S)e^{-i\omega\left(\hat{L}_Z+\hat{S}_Z\right)t}=\ldots=e^{im\omega t}\hat{T}_{lm}(L,S)$$

In other words, the irreducible spherical tensor operators are *eigenoperators* of the $\hat{L}_Z$ commutation superoperator – the consequence of the original spherical harmonics (see the lecture on the $SO(3)$ group) being eigenfunctions of $\hat{L}_Z$.

Consider now the rotating frame transformation of the irreducible spherical tensor expansion of a general Hamiltonian of a coupled two-spin system, in which both spins are of the same type (*e.g.* ^{1}H):

$$\hat{H}=\left[\omega\hat{L}_Z+\omega\hat{S}_Z\right]+\left[\omega_1\hat{L}_Z+\omega_2\hat{S}_Z+2\pi J\left(\hat{L}_X\hat{S}_X+\hat{L}_Y\hat{S}_Y+\hat{L}_Z\hat{S}_Z\right)+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)\right]$$

In a strong enough magnet, the Zeeman frequencies would have two components of very different magnitude – the carrier frequency ω, which is the same for all protons (around 600 MHz in a 14.1 Tesla magnet), and the offset frequencies ω_1, ω_2 coming from the chemical shifts (of the order of kHz in the same magnet). Spin-spin couplings (both isotropic and anisotropic) in typical NMR systems are also in the Hz to kHz range. Based on this observation, we will split the Hamiltonian:

$$\hat{H}=\hat{H}_0+\hat{H}_1,\qquad \hat{H}_0=\omega\hat{L}_Z+\omega\hat{S}_Z$$
$$\hat{H}_1=\omega_1\hat{L}_Z+\omega_2\hat{S}_Z+2\pi J(\hat{\vec{L}}\cdot\hat{\vec{S}})+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)$$

so that the "big" part $\hat{H}_0$ contains the carrier Zeeman frequencies, the "small" part $\hat{H}_1$ has the offsets and the couplings. After the interaction representation transformation with respect to $\hat{H}_0$, we have:

$$\hat{H}_1^{\mathrm{R}}(t)=e^{i\omega\left(\hat{L}_Z+\hat{S}_Z\right)t}\left[\omega_1\hat{L}_Z+\omega_2\hat{S}_Z+2\pi J(\hat{\vec{L}}\cdot\hat{\vec{S}})+\sum_{m=-2}^{2}a_m\hat{T}_{2m}(L,S)\right]e^{-i\omega\left(\hat{L}_Z+\hat{S}_Z\right)t}=$$
$$=\left[\omega_1\hat{L}_Z+\omega_2\hat{S}_Z+2\pi J(\hat{\vec{L}}\cdot\hat{\vec{S}})+a_0\hat{T}_{2,0}(L,S)\right]+\sum_{m\neq0}a_m e^{i\omega mt}\hat{T}_{2m}(L,S)$$

There are two kinds of terms in the resulting rotating frame Hamiltonian – the time-independent terms in square brackets and the very rapidly oscillating (MHz to THz) terms under the sum. The *secular approximation* (dating back to Johannes Kepler, no less) states that the effect of the rapidly oscillating terms may be ignored, because they average to zero on the time scale of the evolution under the time-independent terms (kHz). We will analyse this assumption in detail in due time, but for now we have:

$$\hat{H}_1^{\mathrm{R}} = \omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}} + 2\pi J(\hat{\vec{L}} \cdot \hat{\vec{S}}) + a_0 \hat{T}_{2,0}\left(L,S\right)$$

meaning that the very large terms formally vanish from the Hamiltonian and the time-domain simulation can be carried out in the rotating frame with a fairly leisurely sub-millisecond time step with the additional benefit of not having the double-quantum and mixed terms ($\hat{L}_+\hat{S}_+$, $\hat{L}_{\mathrm{Z}}\hat{S}_+$, *etc.*) around.

Weak coupling limit

The secular Hamiltonian derived in the previous section still contains quite a few terms:

$$\hat{H}_1^{\mathrm{R}} = \omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}} + 2\pi J\left(\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{X}} + \hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{Y}} + \hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}\right) + a_0\sqrt{\frac{2}{3}}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}} - \frac{1}{4}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right)\right)$$

we could take this procedure further and observe that in heteronuclear spin systems the difference in Zeeman frequencies ω_1 and ω_2 is still very large. We could apply a second interaction representation transformation (or amend the original one), with respect to the rest of the Zeeman Hamiltonian:

$$\hat{H}_0 = \omega_1 \hat{L}_{\mathrm{Z}} + \omega_2 \hat{S}_{\mathrm{Z}}$$

$$\hat{H}_1 = \left[\sqrt{\frac{2}{3}}a_0 + 2\pi J\right]\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}} + \left[\pi J - \frac{1}{4}\sqrt{\frac{2}{3}}a_0\right]\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right)$$

It is easy to demonstrate that

$$\begin{array}{c} [\hat{L}_{\mathrm{Z}}, \hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}] = [\hat{S}_{\mathrm{Z}}, \hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}] = [\hat{L}_{\mathrm{Z}}, \hat{S}_{\mathrm{Z}}] = 0 \\ [\hat{L}_{\mathrm{Z}}, \hat{L}_+\hat{S}_-] = -[\hat{S}_{\mathrm{Z}}, \hat{L}_+\hat{S}_-] = \hat{L}_+\hat{S}_- \\ [\hat{L}_{\mathrm{Z}}, \hat{L}_-\hat{S}_+] = -[\hat{S}_{\mathrm{Z}}, \hat{L}_-\hat{S}_+] = -\hat{L}_-\hat{S}_+ \end{array} \quad \Rightarrow \quad \begin{array}{c} e^{i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t}\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}e^{-i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t} = \hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}} \\ e^{i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t}\hat{L}_+\hat{S}_-e^{-i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t} = e^{i\left(\omega_1-\omega_2\right)t}\hat{L}_+\hat{S}_- \\ e^{i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t}\hat{L}_-\hat{S}_+e^{-i\left(\omega_1\hat{L}_{\mathrm{Z}}+\omega_2\hat{S}_{\mathrm{Z}}\right)t} = e^{-i\left(\omega_1-\omega_2\right)t}\hat{L}_-\hat{S}_+ \end{array}$$

and so the second interaction representation transformation yields:

$$\hat{H}_1^{\mathrm{R}} = \left[\sqrt{\frac{2}{3}}a_0 + 2\pi J\right]\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}} + \left[\pi J - \frac{1}{4}\sqrt{\frac{2}{3}}a_0\right]\left(e^{i(\omega_1-\omega_2)t}\hat{L}_+\hat{S}_- + e^{-i(\omega_1-\omega_2)t}\hat{L}_-\hat{S}_+\right)$$

In the cases where the frequency difference $\omega_1 - \omega_2$ is large (that is, in high-field heteronuclear systems), it is permissible to ignore the rapidly oscillating second term, yielding a particularly simple *weak coupling* form for the interaction:

$$\hat{H}_1^{\mathrm{R}} = \left[\sqrt{\frac{2}{3}}a_0 + 2\pi J\right]\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}$$

Pseudosecular coupling

A situation that often occurs in ESR spectroscopy is when only one of the Zeeman interactions is much larger than the spin-spin couplings – in a 0.33 Tesla ESR magnet, the proton Zeeman frequency is just 14 MHz, which is comparable to the typical hyperfine coupling. We can therefore only achieve any simplification by going into the rotating frame with respect to just one of the two coupled spins. We will also need to have the Hamiltonian written out explicitly term by term *via* raising and lowering operators:

$$\hat{H}=\omega_{\mathrm{e}}\hat{L}_{\mathrm{Z}}+\omega_{\mathrm{n}}\hat{S}_{\mathrm{Z}}+a\left(\hat{L}_{\mathrm{X}}\hat{S}_{\mathrm{X}}+\hat{L}_{\mathrm{Y}}\hat{S}_{\mathrm{Y}}+\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}\right)+\sum_{m=-2}^{2}b_m\hat{T}_{2m}\left(L,S\right)=$$

$$=\omega_{\mathrm{e}}\hat{L}_{\mathrm{Z}}+\omega_{\mathrm{n}}\hat{S}_{\mathrm{Z}}+a\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}+\frac{a}{2}\left(\hat{L}_{+}\hat{S}_{-}+\hat{L}_{-}\hat{S}_{+}\right)+\frac{b_{-2}}{2}\hat{L}_{-}\hat{S}_{-}+\frac{b_{2}}{2}\hat{L}_{+}\hat{S}_{+}-$$

$$-\frac{b_1}{2}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{+}+\hat{L}_{+}\hat{S}_{\mathrm{Z}}\right)+\frac{b_{-1}}{2}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{-}+\hat{L}_{-}\hat{S}_{\mathrm{Z}}\right)+b_0\sqrt{\frac{2}{3}}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}-\frac{1}{4}\left(\hat{L}_{+}\hat{S}_{-}+\hat{L}_{-}\hat{S}_{+}\right)\right)$$

where ω_{e} and ω_{n} are the electron and nuclear Zeeman frequencies, a is the isotropic hyperfine coupling and b_m are the irreducible components of the anisotropic hyperfine coupling. An interaction representation transformation with respect to $\hat{H}_0=\omega_{\mathrm{e}}\hat{L}_{\mathrm{Z}}$ then yields:

$$\hat{H}_1^{\mathrm{R}}=\omega_{\mathrm{n}}\hat{S}_{\mathrm{Z}}+a\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}+\frac{a}{2}\left(e^{i\omega_{\mathrm{e}}t}\hat{L}_{+}\hat{S}_{-}+e^{-i\omega_{\mathrm{e}}t}\hat{L}_{-}\hat{S}_{+}\right)+\frac{b_{-2}}{2}e^{-i\omega_{\mathrm{e}}t}\hat{L}_{-}\hat{S}_{-}+\frac{b_{2}}{2}e^{i\omega_{\mathrm{e}}t}\hat{L}_{+}\hat{S}_{+}-$$

$$-\frac{b_1}{2}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{+}+e^{i\omega_{\mathrm{e}}t}\hat{L}_{+}\hat{S}_{\mathrm{Z}}\right)+\frac{b_{-1}}{2}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{-}+e^{-i\omega_{\mathrm{e}}t}\hat{L}_{-}\hat{S}_{\mathrm{Z}}\right)+b_0\sqrt{\frac{2}{3}}\left(\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}-\frac{1}{4}\left(e^{i\omega_{\mathrm{e}}t}\hat{L}_{+}\hat{S}_{-}+e^{-i\omega_{\mathrm{e}}t}\hat{L}_{-}\hat{S}_{+}\right)\right)$$

where the parts that did not acquire a frequency multiplier have been highlighted in blue. Ignoring the rapidly oscillating terms then yields:

$$\hat{H}_1^{\mathrm{R}}=\omega_{\mathrm{n}}\hat{S}_{\mathrm{Z}}+a\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}-\frac{b_1}{2}\hat{L}_{\mathrm{Z}}\hat{S}_{+}+\frac{b_{-1}}{2}\hat{L}_{\mathrm{Z}}\hat{S}_{-}+b_0\sqrt{\frac{2}{3}}\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}$$

and the requirement for the Hamiltonian to be Hermitian further dictates that $b_{-1}=-b_1$, so that:

$$\hat{H}_1^{\mathrm{R}}=\omega_{\mathrm{n}}\hat{S}_{\mathrm{Z}}+\left(b_0\sqrt{\frac{2}{3}}+a\right)\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}+b_{-1}\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{X}}$$

This form is often useful in ESEEM, ENDOR and DNP simulations.

Summary

System	Low-field	High-field homonuclear	High-field heteronuclear	High-field electron-nuclear
Approximation available	*none*	*secular coupling*	*weak coupling*	*pseudosecular coupling*