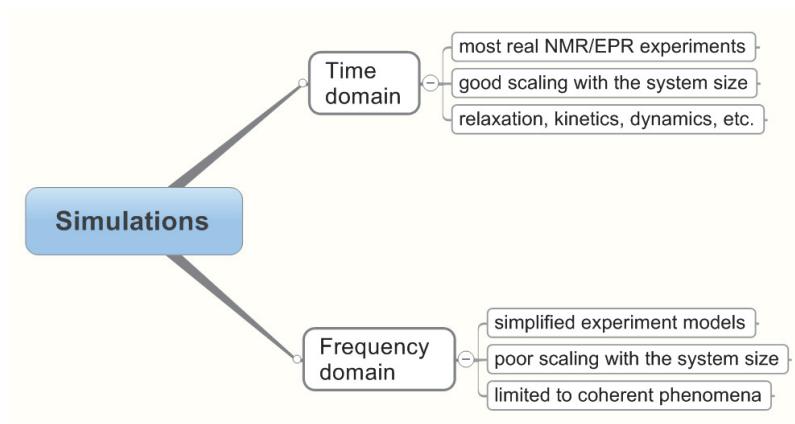
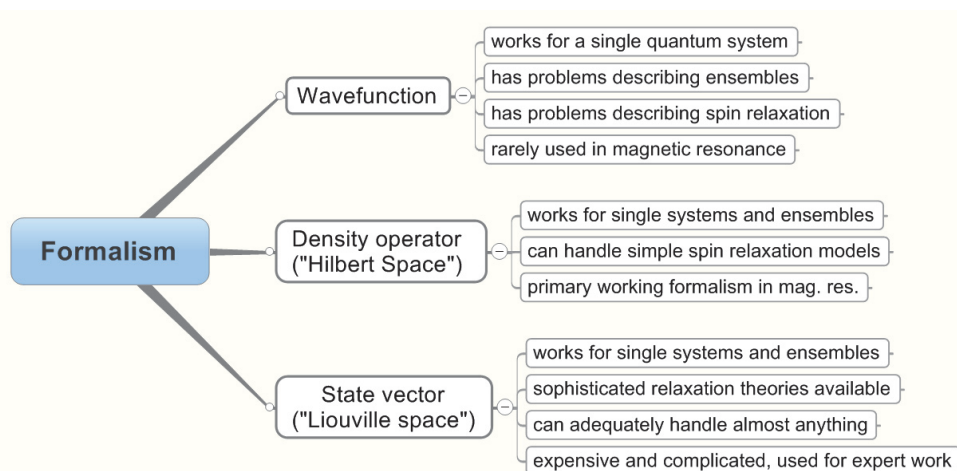


## Module I, Lecture 09: Wavefunction Formalism

From the physical perspective, there are two primary approaches to the simulation of magnetic resonance experiments. In the time-independent formalism (also known as *frequency domain approach*) the Hamiltonian is usually diagonalized and the required properties are obtained from the matrix elements of the various operators in the Hamiltonian eigenbasis. In the time-dependent formalism (also known as *time-domain approach*) the dynamics of the system from a given initial state is calculated forward in time using the Schrodinger equation and the necessary properties are calculated from the time dependence of the expectation values of the operators of interest.



The time domain formalism is more general – at the moment it dominates research-level simulations of magnetic resonance experiments. Frequency domain formalism lingers on in textbooks and simplified experiment descriptions presented in undergraduate quantum theory courses.



The wavefunction approach is based on standard wavefunction mechanics. It is quite educational for small spin systems, but is not well adapted to the treatment of large ensembles of spins – the ensemble average of a wavefunction does often vanish (because wavefunction phases are not required to be the same for different members of the ensemble), even if the observables do not:

$$\overline{e^{i\varphi}\psi(\vec{r},t)} = \overline{e^{i\varphi}\psi(\vec{r},t)} = 0 \quad (1)$$

$$\overline{\langle e^{i\varphi}\psi(\vec{r},t) | \hat{O} | e^{i\varphi}\psi(\vec{r},t) \rangle} = \overline{e^{-i\varphi} e^{i\varphi} \langle \psi(\vec{r},t) | \hat{O} | \psi(\vec{r},t) \rangle} = \langle \psi(\vec{r},t) | \hat{O} | \psi(\vec{r},t) \rangle$$

Still, time-domain solutions to the Schrödinger equation will be useful in later lectures as building blocks for the density operator formalism and relaxation theory.

### Wavefunction formalism, time domain

We shall start by deriving a solution for the time-dependent Schrödinger equation with a static Hamiltonian. After expanding  $|\psi(t)\rangle$  as a Taylor series around  $t = 0$ , we get:

$$|\psi(t)\rangle = |\psi(0)\rangle + \left. \frac{\partial |\psi(t)\rangle}{\partial t} \right|_{t=0} t + \frac{1}{2} \left. \frac{\partial^2 |\psi(t)\rangle}{\partial t^2} \right|_{t=0} t^2 + \frac{1}{6} \left. \frac{\partial^3 |\psi(t)\rangle}{\partial t^3} \right|_{t=0} t^3 + \dots \quad (2)$$

The derivatives of the wavefunction at time zero are known to us from Schrödinger equation:

$$\begin{aligned} \left. \frac{\partial |\psi(t)\rangle}{\partial t} \right|_{t=0} &= -i\hat{H} |\psi(t)\rangle \Big|_{t=0} = -i\hat{H} |\psi(0)\rangle \\ \left. \frac{\partial^2 |\psi(t)\rangle}{\partial t^2} \right|_{t=0} &= \left. \frac{\partial}{\partial t} (-i\hat{H} |\psi(t)\rangle) \right|_{t=0} = (-i\hat{H})^2 |\psi(t)\rangle \Big|_{t=0} = (-i\hat{H})^2 |\psi(0)\rangle \\ \left. \frac{\partial^3 |\psi(t)\rangle}{\partial t^3} \right|_{t=0} &= \dots = (-i\hat{H})^3 |\psi(0)\rangle \end{aligned} \quad (3)$$

and so on. The sum in Equation (2) becomes:

$$|\psi(t)\rangle = |\psi(0)\rangle + (-i\hat{H}t) |\psi(0)\rangle + \frac{1}{2} (-i\hat{H}t)^2 |\psi(0)\rangle + \dots = \left[ \sum_{n=0}^{\infty} \frac{(-i\hat{H}t)^n}{n!} \right] |\psi(0)\rangle \quad (4)$$

It is easy to recognize a Taylor expansion of the exponential function in square brackets. That is, in fact, the definition of an *operator exponential*. With that in place, we get the most general possible solution to the TDSE with a static Hamiltonian:

$$|\psi(t)\rangle = \left[ \sum_{n=0}^{\infty} \frac{(-i\hat{H}t)^n}{n!} \right] |\psi(0)\rangle = \exp(-i\hat{H}t) |\psi(0)\rangle \quad (5)$$

In any matrix representation that makes the solution trivial (although not necessarily fast) to compute.

The case of a time-dependent Hamiltonian is considerably more complicated and uses *Dyson series*, taking into account the fact that the Hamiltonian might not commute with itself at different times:

$$\frac{\partial |\psi(t)\rangle}{\partial t} = -i\hat{H}(t) |\psi(t)\rangle \quad \Rightarrow \quad |\psi(t)\rangle = |\psi(0)\rangle + (-i) \int_0^t \hat{H}(t_1) |\psi(t_1)\rangle dt_1 \quad (6)$$

After applying this recursion relation multiple times, we get:

$$\begin{aligned} |\psi(t)\rangle &= \left[ 1 + (-i) \int_0^t dt_1 \hat{H}(t_1) + (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \hat{H}(t_1) \hat{H}(t_2) + \dots \right] |\psi(0)\rangle = \left[ \sum_{n=0}^{\infty} \hat{U}_n(t) \right] |\psi(0)\rangle \\ \hat{U}_n(t) &= (-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \hat{H}(t_1) \hat{H}(t_2) \dots \hat{H}(t_n) \end{aligned} \quad (7)$$

The upper limits in the integrals are ordered in the sense that  $t \geq t_1 \geq t_2 \geq \dots \geq t_n$ , and this makes the integrals awkward to compute. At the same time, it is known that, for a function  $K(t, t_1, t_2, \dots, t_n)$  that is symmetric in all of its arguments:

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n K(t, t_1, t_2, \dots, t_n) = \frac{1}{n!} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n K(t, t_1, t_2, \dots, t_n) \quad (8)$$

and so we can do a replacement if we can find a way of making  $\hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n)$  product symmetric with respect to the time arguments. Such a way exists, and we will do this by introducing a *time-ordering superoperator*  $\hat{T}$ , which would inspect the order of times in  $\hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n)$  and reorder the Hamiltonians in such a way as to preserve the descending time sequence. This would not have any effect on Equation (7) because the times are already in order there, but it would give us a symmetric operator which we can use to apply Equation (8), because  $\hat{T}[\hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n)]$  is symmetric with respect to all time arguments. After applying this to Equation (7), we get:

$$\begin{aligned} \hat{U}_n(t) &= (-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n) = \\ &= \frac{(-i)^n}{n!} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \hat{T}[\hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n)] = \\ &= \frac{(-i)^n}{n!} \hat{T} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)\dots\hat{H}(t_n) = \frac{1}{n!} \hat{T} \left[ -i \int_0^t \hat{H}(t') dt' \right]^n \end{aligned} \quad (9)$$

Then, after placing this result into the original Dyson series, we obtain:

$$|\psi(t)\rangle = \left[ \sum_{n=0}^{\infty} \hat{U}_n(t) \right] |\psi(0)\rangle = \hat{T} \left[ \sum_{n=0}^{\infty} \frac{1}{n!} \left( -i \int_0^t \hat{H}(t') dt' \right)^n \right] |\psi(0)\rangle \quad (10)$$

where the time-ordering superoperator has been taken out of the bracket. After recognizing the Taylor series for an exponential in the square brackets, we finally obtain:

$$|\psi(t)\rangle = \hat{T} \exp \left( -i \int_0^t \hat{H}(t) dt \right) |\psi(0)\rangle \quad (11)$$

This is the most general possible solution for the time-dependent Schrodinger equation. The rest of time-dependent quantum mechanics is concerned with specific Hamiltonians and with finding efficient methods and approximations to facilitate the practical evaluation of Equations (9)-(11). The time ordering superoperator should be understood in the sense prescribed by Equation (9) – it keeps the Hamiltonian products time-ordered during the integration of the individual terms in the Taylor expansion of the exponential in Equation (11). It should be noted that actual numerical evaluation of Equations (9)-(11) as given above is rarely possible for computational reasons.

In the cases where the Hamiltonian may be assumed to be piecewise-constant, a simpler solution exists, based on the sequential use of Equation (5) for each step in the Hamiltonian:

$$|\psi(t)\rangle = \left[ \prod_k \exp(-i\hat{H}_k \Delta t_k) \right] |\psi(0)\rangle \quad (12)$$

This is currently the preferred way of performing time propagation with time-dependent Hamiltonians, both for reasons of simplicity and because many hardware devices generate continuous waveforms as a sequence of finite steps.

The time evolution of an observable may be computed as the corresponding expectation value. In the case of a static Hamiltonian:

$$\langle A \rangle(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(0) | e^{i\hat{H}t} \hat{A} e^{-i\hat{H}t} | \psi(0) \rangle \quad (13)$$

This equation also illustrates the connection between the Schrödinger formalism and the Heisenberg formalism in wavefunction quantum mechanics.

As an example of a time-domain solution, let us consider a single spin in a magnetic field directed along the Z axis of the laboratory frame. The Hamiltonian is:

$$\hat{H} = \omega \hat{S}_Z \quad \frac{\partial}{\partial t} | \psi \rangle = -i\omega \hat{S}_Z | \psi \rangle \quad (14)$$

The general solution to this problem is obtained using Equation (5):

$$\begin{aligned} e^{-i\omega \hat{S}_Z t} &= \sum_{n=0}^{\infty} \frac{(-i\omega t)^n}{n!} \hat{S}_Z^n = \sum_{n=0}^{\infty} \frac{(-i\omega t)^n}{n!} \begin{pmatrix} (1/2)^n & 0 \\ 0 & (-1/2)^n \end{pmatrix} = \begin{pmatrix} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i\omega t}{2}\right)^n & 0 \\ 0 & \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i\omega t}{2}\right)^n \end{pmatrix} = \\ &= \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \Rightarrow | \psi(t) \rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} | \psi(0) \rangle \end{aligned} \quad (15)$$

If the initial direction of the spin is along the Z axis,

$$| \psi(0) \rangle = | \alpha \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \Rightarrow | \psi(t) \rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} \quad (16)$$

and the time dependence of the three projections of our spin is:

$$\begin{aligned} \langle S_X(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 0 \\ \langle S_Y(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 0 \\ \langle S_Z(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 1/2 \end{aligned} \quad (17)$$

So the magnetization stays on the Z axis. If the initial state is along the X axis:

$$| \psi(0) \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix}^T, \quad \langle \psi(0) | \hat{S}_X | \psi(0) \rangle = 1/2 \quad (18)$$

$$\langle \psi(0) | \hat{S}_Y | \psi(0) \rangle = \langle \psi(0) | \hat{S}_Z | \psi(0) \rangle = 0$$

$$\langle \psi(t) | \hat{S}_Z | \psi(t) \rangle = 0$$

$$| \psi(t) \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2} \end{pmatrix} \Rightarrow \langle \psi(t) | \hat{S}_X | \psi(t) \rangle = \dots = \frac{1}{2} \cos(\omega t) \quad (19)$$

$$\langle \psi(t) | \hat{S}_Y | \psi(t) \rangle = \dots = -\frac{1}{2} \sin(\omega t)$$

then the spin shows the expected circular precession in the XY plane.

## Wavefunction formalism, frequency domain

For systems with a static Hamiltonian, the Schrödinger equation has an easily derived counterpart in the frequency domain:

$$\int_0^{\infty} \frac{\partial}{\partial t} |\psi(t)\rangle e^{-i\omega t} dt = \left( |\psi(t)\rangle e^{-i\omega t} \right) \Big|_0^{\infty} + i\omega \int_0^{\infty} |\psi(t)\rangle e^{-i\omega t} dt = i\omega |\psi(\omega)\rangle - |\psi(0)\rangle = -i\hat{H} |\psi(\omega)\rangle \quad (20)$$

$$i(\hat{H} + \omega\hat{1}) |\psi(\omega)\rangle = |\psi(0)\rangle$$

In most cases, the operator  $\hat{H} + \omega\hat{1}$  is invertible, and therefore:

$$|\psi(\omega)\rangle = -i(\hat{H} + \omega\hat{1})^{-1} |\psi(0)\rangle \quad (21)$$

This equation has a singularity whenever the frequency variable matches one of the Hamiltonian eigenvalues. In practical numerical calculations an extra “damping” term is added to move the probe frequency away from the real axis, thus avoiding the singularity:

$$|\psi(\omega)\rangle = -i(\hat{H} + \omega\hat{1} + ir\hat{1})^{-1} |\psi(0)\rangle \quad (22)$$

$$\langle A \rangle(\omega) = \langle \psi(0) | (\hat{H} + \omega\hat{1} - ir\hat{1})^{-1} \hat{A} (\hat{H} + \omega\hat{1} + ir\hat{1})^{-1} | \psi(0) \rangle$$

where  $r$  is the damping (*aka* “line broadening”) parameter. The calculations are carried forward with this extra term present and the limit of  $r \rightarrow 0$  is taken, if necessary, at the end of the calculation.

A somewhat older approach to computing a frequency-domain absorption spectrum is based on Fermi’s Golden Rule and inspired by the way the early magnetic resonance instruments operated (by monitoring the absorption of a very weak probe field at a given frequency  $\omega$ ). For a given initial and final state, the FGR transition rate under a field with a Hamiltonian  $\hat{V}$  is

$$W_{fi}(\omega) = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(\omega) = \frac{2\pi}{\hbar} |\langle \text{final} | \hat{V} | \text{initial} \rangle|^2 \rho(\omega) \quad (23)$$

where  $|\text{initial}\rangle$  and  $|\text{final}\rangle$  are eigenfunctions of  $\hat{H}$  and  $\rho(\omega)$  is the density of final states at the frequency  $\omega$ . The transition rate in Equation (23) generally has to be computed for every pair of Hamiltonian eigenfunctions.

As an example of a frequency domain solution let us consider a coupled two-spin system with the following Hamiltonian:

$$\begin{aligned} \hat{H} &= \omega_L \hat{L}_Z + \omega_S \hat{S}_Z + J(\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y + \hat{L}_Z \hat{S}_Z) = \dots = \\ &= \omega_L \hat{L}_Z + \omega_S \hat{S}_Z + J \left( \hat{L}_X \hat{S}_X + \frac{1}{2} (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \right) \end{aligned} \quad (24)$$

we have the following transformations for the basis functions  $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ :

$$\begin{aligned} \hat{H} |\alpha\alpha\rangle &= \dots = \left( \frac{\omega_L + \omega_S}{2} + \frac{J}{4} \right) |\alpha\alpha\rangle, & \hat{H} |\alpha\beta\rangle &= \dots = \left( \frac{\omega_L - \omega_S}{2} - \frac{J}{4} \right) |\alpha\beta\rangle + \frac{J}{4} |\beta\alpha\rangle, \\ \hat{H} |\beta\beta\rangle &= \dots = \left( -\frac{\omega_L + \omega_S}{2} + \frac{J}{4} \right) |\beta\beta\rangle, & \hat{H} |\beta\alpha\rangle &= \dots = \left( \frac{\omega_S - \omega_L}{2} - \frac{J}{4} \right) |\beta\alpha\rangle + \frac{J}{4} |\alpha\beta\rangle \end{aligned} \quad (25)$$

So  $|\alpha\alpha\rangle$  and  $|\beta\beta\rangle$  are eigenfunctions already, but the  $\{|\alpha\beta\rangle, |\beta\alpha\rangle\}$  subspace needs to be solved for eigenfunctions. Inside this subspace the Hamiltonian has the following matrix representation:

$$\hat{H}_{\{|\alpha\beta\rangle, |\beta\alpha\rangle\}} = \begin{pmatrix} \frac{\omega_L - \omega_S}{2} - \frac{J}{4} & \frac{J}{4} \\ \frac{J}{4} & \frac{\omega_S - \omega_L}{2} - \frac{J}{4} \end{pmatrix} \quad (26)$$

the eigenvalues and eigenvectors of this matrix are:

$$\lambda = -\frac{J}{4} \pm \frac{\sqrt{J^2 + (\omega_L - \omega_S)^2}}{2} \quad (27)$$

$$\begin{aligned} |\psi_A\rangle &= \cos \varphi |\alpha\beta\rangle + \sin \varphi |\beta\alpha\rangle \\ |\psi_B\rangle &= -\sin \varphi |\alpha\beta\rangle + \cos \varphi |\beta\alpha\rangle \end{aligned} \quad \tan \varphi = \frac{J}{(\omega_L - \omega_S) - \sqrt{J^2 + (\omega_L - \omega_S)^2}}$$

where  $\varphi$  is known as the *mixing angle*. Therefore the four energy values and the corresponding eigenfunctions of the Hamiltonian in Equation (24) are

$$\begin{aligned} \omega_1 &= \left( \frac{\omega_L + \omega_S}{2} + \frac{J}{4} \right) & |1\rangle &= |\alpha\alpha\rangle \\ \omega_2 &= -\frac{J}{4} + \frac{\sqrt{J^2 + (\omega_L - \omega_S)^2}}{2} & |2\rangle &= \cos \varphi |\alpha\beta\rangle + \sin \varphi |\beta\alpha\rangle \\ \omega_3 &= -\frac{J}{4} - \frac{\sqrt{J^2 + (\omega_L - \omega_S)^2}}{2} & |3\rangle &= -\sin \varphi |\alpha\beta\rangle + \cos \varphi |\beta\alpha\rangle \\ \omega_4 &= \left( -\frac{\omega_L + \omega_S}{2} + \frac{J}{4} \right) & |4\rangle &= |\beta\beta\rangle \end{aligned} \quad (28)$$

Finally, after computing the transition frequencies corresponding to the four possible single-spin flips (two-spin flips are forbidden) and the corresponding transition rates under  $\hat{V} = \hat{L}_+ + \hat{S}_+$ , we get:

$$\Delta E = \frac{\omega_L + \omega_S}{2} \pm \frac{J \pm \sqrt{J^2 + (\omega_L - \omega_S)^2}}{2}, \quad \begin{aligned} |\langle 1 | \hat{V} | 3 \rangle|^2 &= |\langle 2 | \hat{V} | 4 \rangle|^2 = \cos^2 \varphi \\ |\langle 1 | \hat{V} | 2 \rangle|^2 &= |\langle 3 | \hat{V} | 4 \rangle|^2 = \sin^2 \varphi \end{aligned} \quad (29)$$

These transition frequencies and intensities correspond to the four signals found in the NMR spectrum of a typical strongly coupled spin system:

