CHEM6154 - Week 23 - Lecture 1: Time-domain quantum mechanics I

P.J. Hore, "NMR: The Toolkit", 1st edition - Chapters 7 and 8.

Solving Schrödinger's equation

We shall start by deriving the general solution for the time-dependent Schrödinger equation

$$\frac{\partial}{\partial t}\psi(t) = -i\hat{H}\psi(t) \tag{1}$$

with a static Hamiltonian. After expanding $\psi(t)$ as a Taylor series around $t=0$, we get:

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

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

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

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

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

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

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

If vector-matrix representations are used for the wavefunction and the Hamiltonian, Dirac brackets appear, and the equations are rewritten as:

$$\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = -i\hat{H}\left|\psi(t)\right\rangle, \qquad \psi(t) = \exp\left(-i\hat{H}t\right)\left|\psi(0)\right\rangle \tag{6}$$

Full quantum mechanical treatment of spin precession

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

$$\hat{H} = \omega\hat{S}_Z \qquad \frac{\partial}{\partial t}\left|\psi\right\rangle = -i\omega\hat{S}_Z\left|\psi\right\rangle \qquad \omega = -\gamma B_0 \tag{7}$$

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

$$\exp\left(-i\omega\hat{S}_{\mathrm{Z}}t\right)=\sum_{n=0}^{\infty}\frac{\left(-i\omega t\right)^{n}}{n!}\hat{S}_{\mathrm{Z}}^{n}=\sum_{n=0}^{\infty}\frac{\left(-i\omega t\right)^{n}}{n!}\begin{pmatrix}\left(1/2\right)^{n} & 0\\ 0 & \left(-1/2\right)^{n}\end{pmatrix}=\begin{pmatrix}e^{-i\omega t/2} & 0\\ 0 & e^{i\omega t/2}\end{pmatrix} \tag{8}$$

and therefore

$$\left|\psi\left(t\right)\right\rangle=\begin{pmatrix}e^{-i\omega t/2} & 0\\ 0 & e^{i\omega t/2}\end{pmatrix}\left|\psi\left(0\right)\right\rangle \tag{9}$$

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

$$\left|\psi\left(0\right)\right\rangle=\left|\alpha\right\rangle=\begin{pmatrix}1\\ 0\end{pmatrix}\quad\Rightarrow\quad\left|\psi\left(t\right)\right\rangle=\begin{pmatrix}e^{-i\omega t/2} & 0\\ 0 & e^{i\omega t/2}\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix}=\begin{pmatrix}e^{-i\omega t/2}\\ 0\end{pmatrix} \tag{10}$$

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

$$\begin{aligned}\left\langle S_{\mathrm{X}}\left(t\right)\right\rangle&=\begin{pmatrix}e^{i\omega t/2} & 0\end{pmatrix}\begin{pmatrix}0 & 1/2\\ 1/2 & 0\end{pmatrix}\begin{pmatrix}e^{-i\omega t/2}\\ 0\end{pmatrix}=0\\ \left\langle S_{\mathrm{Y}}\left(t\right)\right\rangle&=\begin{pmatrix}e^{i\omega t/2} & 0\end{pmatrix}\begin{pmatrix}0 & -i/2\\ i/2 & 0\end{pmatrix}\begin{pmatrix}e^{-i\omega t/2}\\ 0\end{pmatrix}=0\\ \left\langle S_{\mathrm{Z}}\left(t\right)\right\rangle&=\begin{pmatrix}e^{i\omega t/2} & 0\end{pmatrix}\begin{pmatrix}1/2 & 0\\ 0 & -1/2\end{pmatrix}\begin{pmatrix}e^{-i\omega t/2}\\ 0\end{pmatrix}=1/2\end{aligned} \tag{11}$$

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

$$\begin{gathered}\left|\psi\left(0\right)\right\rangle=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\end{pmatrix}^{\mathrm{T}},\qquad\left\langle\psi\left(0\right)\right|\hat{S}_{\mathrm{X}}\left|\psi\left(0\right)\right\rangle=1/2\\ \left\langle\psi\left(0\right)\right|\hat{S}_{\mathrm{Y}}\left|\psi\left(0\right)\right\rangle=\left\langle\psi\left(0\right)\right|\hat{S}_{\mathrm{Z}}\left|\psi\left(0\right)\right\rangle=0\end{gathered} \tag{12}$$

then the corresponding time-dependent solution is

$$\left|\psi\left(t\right)\right\rangle=\frac{1}{\sqrt{2}}\begin{pmatrix}e^{-i\omega t/2} & 0\\ 0 & e^{i\omega t/2}\end{pmatrix}\begin{pmatrix}1\\ 1\end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix}e^{-i\omega t/2}\\ e^{i\omega t/2}\end{pmatrix}\quad\Rightarrow\quad\begin{aligned}&\left\langle\psi\left(t\right)\right|\hat{S}_{\mathrm{Z}}\left|\psi\left(t\right)\right\rangle=0\\ &\left\langle\psi\left(t\right)\right|\hat{S}_{\mathrm{X}}\left|\psi\left(t\right)\right\rangle=\ldots=\frac{1}{2}\cos\left(\omega t\right)\\ &\left\langle\psi\left(t\right)\right|\hat{S}_{\mathrm{Y}}\left|\psi\left(t\right)\right\rangle=\ldots=-\frac{1}{2}\sin\left(\omega t\right)\end{aligned} \tag{13}$$

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

Density operator formalism

We will now build an equivalent formalism based on the dynamics of the corresponding projection operator, commonly called the *density operator*

$$\hat{\rho}\left(t\right)=\left|\psi\left(t\right)\right\rangle\left\langle\psi\left(t\right)\right| \tag{14}$$

It is an operator because it can act upon a wavefunction and return another wavefunction:

$$\hat{\rho}\left|\varphi\right\rangle=\left|\psi\right\rangle\left\langle\psi\middle|\varphi\right\rangle=a\left|\psi\right\rangle,\qquad a=\left\langle\psi\middle|\varphi\right\rangle \tag{15}$$

As defined in Equation (14), it is also an idempotent operator, that is:

$$\hat{\rho}^{2}=\left|\psi\right\rangle\left\langle\psi\middle|\psi\right\rangle\left\langle\psi\right|=\left|\psi\right\rangle\left\langle\psi\right|=\hat{\rho} \tag{16}$$

The equation of motion for $\hat{\rho}(t)$ (called *Liouville – von Neumann equation*) is easily obtained from the definition in Equation (14) and the Schrödinger equation:

$$\frac{\partial}{\partial t}\hat{\rho}(t)=\frac{\partial}{\partial t}\left(|\psi(t)\rangle\langle\psi(t)|\right)=\left(\frac{\partial}{\partial t}|\psi(t)\rangle\right)\langle\psi(t)|+|\psi(t)\rangle\left(\frac{\partial}{\partial t}\langle\psi(t)|\right)=\left\{\begin{matrix}\text{use Schrodinger}\\ \text{equation}\end{matrix}\right\}$$
$$=-i\hat{H}(t)|\psi(t)\rangle\langle\psi(t)|+i|\psi(t)\rangle\langle\psi(t)|\hat{H}(t)=-i\hat{H}\hat{\rho}+i\hat{\rho}\hat{H}=-i\left[\hat{H}(t),\hat{\rho}(t)\right] \tag{17}$$
$$\frac{\partial}{\partial t}\hat{\rho}(t)=-i\left[\hat{H}(t),\hat{\rho}(t)\right]$$

This equation of motion inherits its solutions from the Schrödinger equation:

$$|\psi(t)\rangle=\exp\left[-i\hat{H}t\right]|\psi(0)\rangle$$
$$\Downarrow$$
$$|\psi(t)\rangle\langle\psi(t)|=\exp\left[-i\hat{H}t\right]|\psi(0)\rangle\langle\psi(0)|\exp\left[+i\hat{H}t\right] \tag{18}$$
$$\Downarrow$$
$$\hat{\rho}(t)=\exp\left[-i\hat{H}t\right]\hat{\rho}(0)\exp\left[+i\hat{H}t\right]$$

The calculation of observables similarly undergoes only a cosmetic alteration:

$$\langle A\rangle=\langle\psi|\hat{A}|\psi\rangle=\mathrm{Tr}\left(\langle\psi|\hat{A}|\psi\rangle\right)=\mathrm{Tr}\left(\hat{A}|\psi\rangle\langle\psi|\right)=\mathrm{Tr}\left(\hat{A}\hat{\rho}\right) \tag{19}$$

where we have used the fact that cyclic permutations of products are allowed under the trace:

$$\mathrm{Tr}(\mathbf{ABC})=\mathrm{Tr}(\mathbf{CAB})=\mathrm{Tr}(\mathbf{BCA}) \tag{20}$$

It does therefore appear that the formalism around the density operator defined in Equation (14) is in every respect equivalent to the original wavefunction formalism. There are two primary reasons why this description is often preferred in spin dynamics simulations:

1. $|\psi\rangle$ does not survive the ensemble average, whereas $|\psi\rangle\langle\psi|$ does:

$$\overline{|\psi\rangle}=\frac{1}{2\pi}\int_0^{2\pi}e^{i\varphi}|\psi\rangle d\varphi=0,\qquad \overline{|\psi\rangle\langle\psi|}=\frac{1}{2\pi}\int_0^{2\pi}e^{i\varphi}|\psi\rangle\langle\psi|e^{-i\varphi}d\varphi=|\psi\rangle\langle\psi| \tag{21}$$

2. $|\psi\rangle$ becomes unacceptably large for ~10^{23} spins, whereas the above mentioned ensemble average provides a serviceable substitute to the explicit description for $|\psi\rangle\langle\psi|$.

The physical meaning of $\hat{\rho}(t)$ can be glimpsed from the expressions for its matrix elements. The diagonal elements

$$\langle n|\hat{\rho}|n\rangle=\langle n|\psi\rangle\langle\psi|n\rangle=\left|\langle\psi|n\rangle\right|^2=\left|c_n\right|^2=p_n \tag{22}$$

correspond to the probability of finding the system in a state $|n\rangle$ and the off-diagonal elements indicate the presence of a superposition in the wavefunction:

$$|\psi\rangle=...+c_n|n\rangle+c_k|k\rangle+...$$
$$\hat{\rho}=|\psi\rangle\langle\psi|=\left(...+c_n|n\rangle+c_k|k\rangle+...\right)\left(...+c_n^*\langle n|+c_k^*\langle k|+...\right)=$$
$$=...\left|c_n\right|^2|n\rangle\langle n|+c_nc_k^*|n\rangle\langle k|+c_kc_n^*|k\rangle\langle n|+\left|c_k\right|^2|k\rangle\langle k|+... \tag{23}$$
$$\langle n|\hat{\rho}|k\rangle=c_nc_k^*$$