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Research Article

Quantum Derivation of the Bloch Equations Excluding Relaxation

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The equation of motion of the density matrix of an ensemble of identical spin-1/2 nuclei subject to a rotating-frame radio-frequency field and Zeeman frequency offset is derived from the Schrodinger equation and shown to be equivalent to the magnetization differential equations originally proposed by Bloch (excluding relaxation). The quantum and classical differential equations are then integrated.

1. Introduction

It is well known that the magnetization differential equations (excluding relaxation) of Bloch [1] have a quantum counterpart [2] in the equation of motion of the density matrix under an appropriate Hamiltonian operator. A compact derivation of this equation is presented, and the resulting quantum and classical differential equations are then integrated. The aim throughout is to explicitly illustrate the use of quantum-mechanical principles and matrix methods in formulating and solving this problem. Dirac notation is used to more transparently visualize matrix structures and manipulations. The reader may find it useful to refer first to the overview of Section 3 before beginning Section 2.

2. Theory and Results

2.1. Derivation of the General Equation of Motion of the Density Matrix. The Schrodinger equation in Dirac notation [3] is

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = -i\mathbf{H}|\psi(t)\rangle. \tag{1}$$

$\mathbf{H}$ is a time-independent Hermitian operator (square matrix) and $|\psi(t)\rangle$ is a ket (normalized column vector) state function [4]. The corresponding equation for the adjoint bra $\langle\psi(t)|$ (the row vector complex conjugate transpose) is

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)| = \langle\psi(t)|i\mathbf{H}, \tag{2}$$

making use of the self-adjoint property $\mathbf{H}^{\dagger} = \mathbf{H}$ of a Hermitian matrix.

For an ensemble of identical particles, the outer product of the ket and bra,

$$|\psi(t)\rangle\langle\psi(t)| = \sigma(t), \tag{3}$$

is a matrix $\sigma(t)$ referred to as the density matrix or operator. The time dependence of the density matrix is calculated by differentiating equation (3).

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sigma(t) &= \frac{\mathrm{d}}{\mathrm{d}t}(|\psi(t)\rangle\langle\psi(t)|)\\ &= \frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle\langle\psi(t)| + |\psi(t)\rangle\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)|\\ &= -i\mathbf{H}\sigma(t) + \sigma(t)i\mathbf{H}\\ &= -i(\mathbf{H}\sigma(t) - \sigma(t)\mathbf{H}) = -i[\mathbf{H}, \sigma(t)],\end{aligned} \tag{4}$$

obtained using equations (1), (2), and commutator notation.

Equation (4) is known as the Liouville–von Neumann equation of motion of the density matrix.

2.2. Form of the Density Matrix. The density matrix elements for a spin−1/2 ensemble are constructed from the expectation values of the spin angular momentum operators I_x, I_y, or I_z. These are given by the trace (sum of diagonal elements) of the product of the relevant spin angular momentum operator I_x, I_y, or I_z and the density matrix σ and expressed as ensemble projections $\bar{s}_x$, $\bar{s}_y$ or $\bar{s}_z$of the appropriate angular momentum in half-integer units [4, 5].

$$\langle I_x \rangle = \mathrm{Tr} I_x \sigma = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{pmatrix} = \frac{1}{2} \left(\sigma_{12} + \sigma_{21} \right) = \frac{1}{2} \bar{s}_x, \tag{5}$$

$$\langle I_y \rangle = \mathrm{Tr} I_y \sigma = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{pmatrix} = \frac{i}{2} \left(\sigma_{12} - \sigma_{21} \right) = \frac{1}{2} \bar{s}_y, \tag{6}$$

$$\langle I_z \rangle = \mathrm{Tr} I_z \sigma = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{pmatrix} = \frac{1}{2} \left(\sigma_{11} - \sigma_{22} \right) = \frac{1}{2} \bar{s}_z. \tag{7}$$

Additionally, the trace of the density matrix $\mathrm{Tr}\sigma = \sigma_{11} + \sigma_{22} = 1$. Solving for individual density matrix elements σ is found to be

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + \bar{s}_z & \bar{s}_x - i\bar{s}_y \\ \bar{s}_x + i\bar{s}_y & 1 - \bar{s}_z \end{pmatrix}. \tag{8}$$

The density matrix is Hermitian with diagonal elements proportional classically to longitudinal z-magnetization and off-diagonal elements proportional to (complex) transverse magnetization [2, 5]. It is idempotent ($\sigma^2 = \sigma$) as verified by matrix multiplication using $\bar{s}_x^2 + \bar{s}_y^2 + \bar{s}_z^2 = 1$ for a pure state and $\mathrm{Tr}\sigma^2 = 1$. A geometric formulation of the density matrix is also given in the Appendix. It suffices henceforth to omit the diagonal constant and proportionality factor in equation (8) and express the density matrix as

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{pmatrix} = \begin{pmatrix} \langle I_z \rangle & \langle I_x \rangle - i \langle I_y \rangle \\ \langle I_x \rangle + i \langle I_y \rangle & -\langle I_z \rangle \end{pmatrix}, \tag{8a}$$

with $\langle I_x \rangle^2 + \langle I_y \rangle^2 + \langle I_z \rangle^2 = 1$.

2.3. Form of the Hamiltonian Operator. For a rotating-frame radiofrequency field $\omega_1 = \gamma B_1$ (rad/s) along the x-axis and a (positive) Zeeman frequency offset $\Delta = \omega_{rf} - \omega_0$ (rad/s), the Hamiltonian operator $\mathbf{H}$ is given by

$$\mathbf{H} = \omega_1 I_x + \Delta I_z = \frac{1}{2} \begin{pmatrix} \Delta & \omega_1 \\ \omega_1 & -\Delta \end{pmatrix}. \tag{9}$$

2.4. Evaluation of the Equation of Motion Equation (4). Using the density matrix σ of equation (8a) and the Hamiltonian operator $\mathbf{H}$ of equation (9) in equation (4), we find

$$\frac{\mathrm{d}}{\mathrm{d}t} \sigma = \begin{pmatrix} \omega_1 \langle I_y \rangle & -i\Delta \left(\langle I_x \rangle - i \langle I_y \rangle \right) + i\omega_1 \langle I_z \rangle \\ i\Delta \left(\langle I_x \rangle + i \langle I_y \rangle \right) - i\omega_1 \langle I_z \rangle & -\omega_1 \langle I_y \rangle \end{pmatrix}. \tag{10}$$

Then, $(\mathrm{d}/\mathrm{d}t)\langle I_\alpha \rangle = \mathrm{Tr} I_\alpha (\mathrm{d}/\mathrm{d}t)\sigma \, (\alpha = x, y, z)$ and

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle I_x \rangle = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}t} \sigma = -\Delta \langle I_y \rangle, \tag{11}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle I_y \rangle = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}t} \sigma = \Delta \langle I_x \rangle - \omega_1 \langle I_z \rangle, \tag{12}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle I_z \rangle = \mathrm{Tr} \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}t} \sigma = \omega_1 \langle I_y \rangle. \tag{13}$$

Equations (11)–(13) may be assembled in the matrix form

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_z \rangle \end{pmatrix} = \begin{pmatrix} 0 & -\Delta & 0 \\ \Delta & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{pmatrix} \begin{pmatrix} \langle I_x \rangle \\ \langle I_y \rangle \\ \langle I_z \rangle \end{pmatrix}. \tag{14}$$

As the expectation values are proportional to magnetizations, equations (11)–(13) are seen to be equivalent to the coupled differential equations of Bloch [1]. They may also be written in a compact form $(d/dt)\langle I_\alpha\rangle = -i\langle [I_\alpha, \mathbf{H}]\rangle$ using the cyclic commutation relations $[I_\alpha, I_\beta] = iI_\gamma$ of the spin operators [2].

2.5. Superoperator Form of the Liouville–von Neumann Equation. A commutator superoperator Γ can also be constructed from $\mathbf{H}$ using direct products [4].

$$\Gamma = \mathbf{H}\otimes E - E\otimes\mathbf{H} = \frac{1}{2}\begin{pmatrix} \Delta & \omega_1 \\ \omega_1 & -\Delta \end{pmatrix}\otimes\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\otimes\begin{pmatrix} \Delta & \omega_1 \\ \omega_1 & -\Delta \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 & -\omega_1 & \omega_1 & 0 \\ -\omega_1 & 2\Delta & 0 & \omega_1 \\ \omega_1 & 0 & -2\Delta & -\omega_1 \\ 0 & \omega_1 & -\omega_1 & 0 \end{pmatrix}. \tag{15}$$

If the elements of σ in equation (8a) are arrayed as a column supervector $\hat{\sigma}$, equation (4) becomes

$$\frac{d}{dt}\hat{\sigma} = -i\Gamma\hat{\sigma} = -\frac{i}{2}\begin{pmatrix} 0 & -\omega_1 & \omega_1 & 0 \\ -\omega_1 & 2\Delta & 0 & \omega_1 \\ \omega_1 & 0 & -2\Delta & -\omega_1 \\ 0 & \omega_1 & -\omega_1 & 0 \end{pmatrix}\begin{pmatrix} \langle I_z\rangle \\ \langle I_x\rangle - i\langle I_y\rangle \\ \langle I_x\rangle + i\langle I_y\rangle \\ -\langle I_z\rangle \end{pmatrix}. \tag{16}$$

By solving $(d/dt)\langle I_x\rangle, (d/dt)\langle I_y\rangle$ and $(d/dt)\langle I_z\rangle$, we obtain equations (11)–(13).

2.6. Integration of the Equation of Motion Equation (4). The integrated solutions of Schrodinger equations (1), (2) are

$$|\psi(t)\rangle = \exp(-i\mathbf{H}t)|\psi(0)\rangle, \tag{17}$$

$$\langle\psi(t)| = \langle\psi(0)|\exp i\mathbf{H}t. \tag{18}$$

Accordingly

$$\begin{aligned}\sigma(t) = |\psi(t)\rangle\langle\psi(t)| &= \exp(-i\mathbf{H}t)|\psi(0)\rangle\langle\psi(0)|\exp i\mathbf{H}t \\ &= \exp(-i\mathbf{H}t)\sigma(0)\exp i\mathbf{H}t.\end{aligned} \tag{19}$$

Equation (19) provides a means of calculating the time evolution of the density matrix (unitary transformation) from some initial state with the exponential operator $\exp(-i\mathbf{H}t)$ and its adjoint.

Equation (4) may be recovered by differentiating equation (19), as follows:

$$\begin{aligned}\frac{d}{dt}\sigma(t) &= -i\mathbf{H}\sigma(t) + \exp(-i\mathbf{H}t)\sigma(0)i\mathbf{H}\exp i\mathbf{H}t \\ &= -i\mathbf{H}\sigma(t) + \sigma(t)i\mathbf{H} = -i[\mathbf{H}, \sigma(t)],\end{aligned} \tag{20}$$

as $\mathbf{H}$ and $\exp i\mathbf{H}t$ commute.

2.7. Form of the Exponential Operator $\mathbf{R} = \exp - i\mathbf{H}t$. As I_x and I_z do not commute the operator $\exp - i\mathbf{H}t$ must be explicitly calculated.

The diagonal matrix of eigenvalues of the Hamiltonian operator $\mathbf{H}$ of equation (9) is

$$\mathbf{D} = \frac{1}{2}\begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix}, \quad \Omega = \left(\Delta^2 + \omega_1^2\right)^{1/2}. \tag{21}$$

The corresponding normalized eigenvector matrix $\mathbf{U}$ is found to be

$$\mathbf{U} = \begin{pmatrix} \cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & \cos(\theta/2) \end{pmatrix} = (\,|1\rangle\ \ |2\rangle\,), \tag{22}$$

with $\tan\theta = (\omega_1/\Delta)$ and expressing $\mathbf{U}$ as a row vector of kets.

As $\mathbf{U}$ is unitary $\mathbf{U}^T = \mathbf{U}^{-1}$ and $\mathbf{H} = \mathbf{UDU}^{-1}$. The operator $\mathbf{R} = \exp - i\mathbf{H}t$ is then given by

$$\begin{aligned}\mathbf{R} = \mathbf{U}\exp(-i\mathbf{D}t)\mathbf{U}^{-1} &= (\,|1\rangle\ \ |2\rangle\,)\begin{pmatrix} (c - is)\langle 1| \\ (c + is)\langle 2| \end{pmatrix} \\ &= c(|1\rangle\langle 1| + |2\rangle\langle 2|) - is(|1\rangle\langle 1| - |2\rangle\langle 2|) \\ &= \begin{pmatrix} c - is\cos\theta & -is\sin\theta \\ -is\sin\theta & c + is\cos\theta \end{pmatrix} = (\,|1\rangle\ \ |2\rangle\,),\end{aligned} \tag{23}$$

using half-angle formulas with $c, s = \cos(\Omega/2)t, \sin(\Omega/2)t$ and expressing $\mathbf{R}$ as a row vector of kets. As $\mathbf{R}$ is unitary, the adjoint is given by

$$\begin{aligned}\mathbf{R}^\dagger = \mathbf{R}^{-1} = \exp i\mathbf{H}t &= \begin{pmatrix} c + is\cos\theta & is\sin\theta \\ is\sin\theta & c - is\cos\theta \end{pmatrix} \\ &= \begin{pmatrix} \langle 1| \\ \langle 2| \end{pmatrix},\end{aligned} \tag{24}$$

using Dirac notation to write $\mathbf{R}^\dagger$ as the corresponding column vector of bras.

2.8. Time Evolution of the Density Matrix for Various Initial States. (a) With the system initially at equilibrium $\langle I_z\rangle = 1$ and the density matrix of equation (8a) evolves according to equation (19). Using Dirac notation for $\mathbf{R}$ and $\mathbf{R}^\dagger$, we may write

$$\begin{aligned}\sigma(t) &= \mathbf{R}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\mathbf{R}^\dagger = |1\rangle\langle 1| - |2\rangle\langle 2|\\ &= \begin{pmatrix}\cos^2\theta + c\,\sin^2\theta & is\sin\theta + \sin\theta\cos\theta[1-c]\\ -is\sin\theta + \sin\theta\cos\theta[1-c] & -\cos^2\theta - c\,\sin^2\theta\end{pmatrix},\end{aligned} \tag{25}$$

using half-angle formulas and now with $c, s = \cos\Omega t, \sin\Omega t$ (the reader should verify equations (23) and (25)). The trace expressions of equations (5)–(7) then provide the integrated solutions

$$\langle I_x\rangle = \sin\theta\cos\theta\,[1-\cos\Omega t], \tag{26}$$

$$\langle I_y\rangle = -\sin\theta\,\sin\Omega t, \tag{27}$$

$$\langle I_z\rangle = \cos^2\theta + \sin^2\theta\,\cos\Omega t. \tag{28}$$

(b) With the system initially along $x\langle I_x\rangle = 1$ and $\sigma(t) = \mathbf{R}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\mathbf{R}^\dagger = |1\rangle\langle 2| + |2\rangle\langle 1|$. Along $y\langle I_y\rangle = 1$ and $\sigma(t) = \mathbf{R}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\mathbf{R}^\dagger = -i(|1\rangle\langle 2| - |2\rangle\langle 1|)$. These equations lead, respectively, to sets of expectation values given by column 1 or column 2 of equation (42).

(c) For $\langle I_x\rangle = \sin\theta$ and $\langle I_z\rangle = \cos\theta$, the ensemble is aligned with the effective field $B_{\text{eff}} = (\Omega/\gamma)$ and σ is time-independent (the reader should verify this assertion).

2.9. Radiofrequency Field along the y-Axis. For a rf field along the y-axis, the Hamiltonian operator $\mathbf{H}$ becomes

$$\mathbf{H} = \omega_1 I_y + \Delta I_z = \frac{1}{2}\begin{pmatrix}\Delta & -i\omega_1\\ i\omega_1 & -\Delta\end{pmatrix}. \tag{29}$$

The eigenvalues are again those of equation (21), and $\mathbf{U}$ is found to be

$$\mathbf{U} = \begin{pmatrix}\cos(\theta/2) & -\sin(\theta/2)\\ i\sin(\theta/2) & i\cos(\theta/2)\end{pmatrix} = (|1\rangle\ \ |2\rangle), \tag{30}$$

from which $\mathbf{R}$ is calculated from equation (23) using equation (30) and its adjoint to be

$$\begin{aligned}\mathbf{R} &= \exp - i\mathbf{H}t = \mathbf{U}\exp(-i\mathbf{D}t)\mathbf{U}^\dagger\\ &= \begin{pmatrix}c - is\cos\theta & -s\sin\theta\\ s\sin\theta & c + is\cos\theta\end{pmatrix} = (|1\rangle\ \ |2\rangle),\end{aligned} \tag{31}$$

using half-angle formulas with $c, s = \cos(\Omega/2)t, \sin(\Omega/2)t$ and writing $\mathbf{R}$ as a row vector of kets.

With $\langle I_z\rangle = 1$, the density matrix evolves using equation (31) and its adjoint $\mathbf{R}^\dagger$ according to

$$\begin{aligned}\sigma(t) &= \mathbf{R}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\mathbf{R}^\dagger = |1\rangle\langle 1| - |2\rangle\langle 2|\\ &= \begin{pmatrix}\cos^2\theta + c\,\sin^2\theta & s\,\sin\theta - i\,\sin\theta\cos\theta[1-c]\\ s\,\sin\theta + i\sin\theta\,\cos\theta[1-c] & -\cos^2\theta - c\,\sin^2\theta\end{pmatrix},\end{aligned} \tag{32}$$

using half-angle formulas and now with $c, s = \cos \Omega t, \sin \Omega t$.

Equations (5)–(7) give the integrated solutions

$$\langle I_x \rangle = \sin\theta \sin \Omega t, \quad (33)$$

$$\langle I_y \rangle = \sin\theta \cos\theta [1 - \cos \Omega t], \quad (34)$$

$$\langle I_z \rangle = \cos^2\theta + \sin^2\theta \cos \Omega t. \quad (35)$$

2.10. Integration of the Bloch Differential Equations. Equation (14) may be recast as

$$\frac{d}{dt}\mathbf{M} = -\mathbf{K}\mathbf{M}, \quad (36)$$

where $\mathbf{M} = \begin{pmatrix} M_x & M_y & M_z \end{pmatrix}^T$ is a column vector of magnetizations and

$$\mathbf{K} = \begin{pmatrix} 0 & \Delta & 0 \\ -\Delta & 0 & \omega_1 \\ 0 & -\omega_1 & 0 \end{pmatrix}. \quad (37)$$

The integrated solution is

$$\mathbf{M}(t) = \exp(-\mathbf{K}t)\mathbf{M}(0). \quad (38)$$

The diagonal eigenvalue matrix of $\mathbf{K}$ is $\mathbf{D} = \operatorname{diag}\begin{pmatrix} 0 & i\Omega & -i\Omega \end{pmatrix} \Omega = (\Delta^2 + \omega_1^2)^{1/2}$, and the normalized eigenvector matrix $\mathbf{U}$ that diagonalizes $\mathbf{K}$ is found to be

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{2}\sin\theta & \cos\theta & \cos\theta \\ 0 & i & -i \\ \sqrt{2}\cos\theta & -\sin\theta & -\sin\theta \end{pmatrix} = \begin{pmatrix} |1> & |2> & \lfloor 3> \end{pmatrix}, \quad (39)$$

expressing $\mathbf{U}$ as a row vector of kets. As $\mathbf{U}$ is unitary, the matrix adjoint $\mathbf{U}^\dagger = \mathbf{U}^{-1}$, the corresponding column vector of bras. Using Dirac notation, diagonalization of $\mathbf{K}$ can be represented as

$$\mathbf{U}^{-1}\mathbf{K}\mathbf{U} = \begin{pmatrix} \langle 1| \\ \langle 2| \\ \langle 3| \end{pmatrix} \begin{pmatrix} 0|1\rangle & i\Omega|2\rangle & -i\Omega|3\rangle \end{pmatrix} = \begin{pmatrix} 0 & & \\ & i\Omega & \\ & & -i\Omega \end{pmatrix} = \mathbf{D}, \quad (40)$$

where, e.g., $|i\rangle$ represents the ith column of $\mathbf{U}$, $\langle i|$ is its row adjoint, $\langle i|i\rangle = 1$, and $\langle i|j\rangle = 0$.

$\mathbf{K}$ is given by

$$\mathbf{K} = \mathbf{U}\,\mathbf{D}\mathbf{U}^{-1} = \begin{pmatrix} |1\rangle & |2\rangle & |3\rangle \end{pmatrix} \begin{pmatrix} 0 & & \\ & i\Omega & \\ & & -i\Omega \end{pmatrix} \begin{pmatrix} \langle 1| \\ \langle 2| \\ \langle 3| \end{pmatrix} = i\Omega(|2\rangle\langle 2| - |3\rangle\langle 3|). \quad (41)$$

The matrix $\mathbf{A} = \exp - \mathbf{K}t$ is then

$$\begin{aligned} \mathbf{A} &= \mathbf{U}\exp - \mathbf{D}t\mathbf{U}^{-1} = \begin{pmatrix} |1\rangle & |2\rangle & \lfloor 3\rfloor \end{pmatrix} \begin{pmatrix} \langle 1| \\ (c - is)\langle 2| \\ (c + is)\langle 3| \end{pmatrix} \\ &= |1\rangle\langle 1| + c(|2\rangle\langle 2| + |3\rangle\langle 3|) - is(|2\rangle\langle 2| - |3\rangle\langle 3|) \\ &= \begin{pmatrix} \sin^2\theta + c\cos^2\theta & -s\cos\theta & \sin\theta\cos\theta[1-c] \\ s\cos\theta & c & -s\sin\theta \\ \sin\theta\cos\theta[1-c] & s\sin\theta & \cos^2\theta + c\sin^2\theta \end{pmatrix}, \end{aligned} \quad (42)$$

with $c, s = \cos \Omega t, \sin \Omega t$ (the reader should verify equation (42)).

$\mathbf{K}$ is antisymmetric so that $\mathbf{K}^T = -\mathbf{K}$, $(\exp - \mathbf{K}t)^T = (\exp \mathbf{K}t)$ and $(\exp - \mathbf{K}t)(\exp - \mathbf{K}t)^T = E$. $\mathbf{A}$ is therefore orthogonal and $\langle i|i\rangle = 1$, $\langle i|j\rangle = 0$.

Equation (38) becomes

$$\mathbf{M}(t) = \mathbf{A}\mathbf{M}(0). \quad (43)$$

For the system initially at equilibrium, $\mathbf{M}(0) = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix}^T$ and $\mathbf{M}(t)$ is given by column 3 of equation (42). These solutions are those of equations (26)–(28) obtained by integration of the density matrix.

3. Discussion

The results of Section 2 are summarized here to delineate the steps leading from the Schrodinger eq. (1) to the differential eq. (14) of the expectation values of the spin angular momentum operators and their subsequent integration.

(1) The general differential equation of motion of the density matrix equation (4) is first derived from the Schrodinger equation (1) and its adjoint equation (2).

(2) The density matrix equation (8) for an ensemble of identical spin−1/2 nuclei is then constructed from the expectation values of the spin angular momentum operators.

(3) The Hamiltonian operator equation (9) for a rotating-frame rf field and Zeeman frequency offset is formulated.

(4) The time dependence of the density matrix elements is then calculated (equation (10)). Suitable combinations of these give coupled differential equations (11)–(13) for the expectation values of the spin operators.

(5) An equivalent superoperator formulation of the equation of motion is presented.

(6) Integration of the Schrodinger equations (1), (2) leads to equation (19) describing the time evolution of the density matrix via unitary transformation using an exponential operator and its adjoint.

(7) A diagonalization method is used to calculate the necessary exponential operator (equation (23)).

(8) The time evolution of the density matrix equation (19) is then calculated for the Hamiltonian operator of equation (9) with the initial condition $\langle I_z \rangle = 1$, and suitable combinations of density matrix elements give equations (26)–(28) for the spin operator expectation values. Other initial conditions are considered.

(9) A shifted rf field along the y-axis (equation (29)) leads to expectation values given by equations (33)–(35) for the system initially at equilibrium.

(10) Finally, a diagonalization method is used to integrate the Bloch differential equation (36), giving equation (43).

4. Conclusion

As the expectation values of the operators representing the projection of the spin angular momentum along x, y or z are proportional to the respective magnetizations, the quantum and classical differential equations of motion (and their integrated solutions) for a spin−1/2 ensemble are shown to be equivalent. It is noteworthy that the Bloch equations, originally proposed phenomenologically [1] using a classical argument, are quantum-mechanical in origin. The equivalence arises from the correspondence [2] between (a) the (classical) cross product coupling of the nuclear magnetic moment vector with the effective field vector and (b) the (quantum-mechanical) commutation relations governing the spin angular momentum operators used to construct the density matrix and the effective field Hamiltonian operator.

Appendix

The state of the spin−1/2 ensemble may be represented by the general linear operator

$$\mathbf{O} \propto \bar{s}_x I_x + \bar{s}_y I_y + \bar{s}_z I_z$$

&9; $= \begin{pmatrix} \cos\theta & \sin\theta \\ \sin^*\theta & -\cos\theta \end{pmatrix},$ (A.1)

with $\tan\theta = (|\bar{s}_x - i\bar{s}_y|/\bar{s}_z)$ and $\bar{s}_x^2 + \bar{s}_y^2 + \bar{s}_z^2 = 1$. The symbol * denotes complex conjugate.

The unitary eigenvector matrix $\mathbf{U}$ that diagonalizes $\mathbf{O}$ is found to be

$$\mathbf{U} = \begin{pmatrix} c & -s \\ s^* & c^* \end{pmatrix} = \begin{pmatrix} |1\rangle & |2\rangle \end{pmatrix}, \quad s = \sin\left(\frac{\theta}{2}\right), c = \cos\left(\frac{\theta}{2}\right), \tag{A.2}$$

with corresponding eigenvalues ±1. The density matrix is then

$$\sigma = \begin{pmatrix} cc^* & cs \\ (cs)^* & ss^* \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 + \cos\theta & \sin\theta \\ \sin^*\theta & 1 - \cos\theta \end{pmatrix}, \tag{A.3}$$

in agreement with equation (8). The idempotent nature of σ is evident as $\sigma^2 = |1\rangle\langle 1||1\rangle\langle 1| = |1\rangle\langle 1| = \sigma$.

Data Availability

There are no data accompanying this research article.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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