Progress in Nuclear Magnetic Resonance Spectroscopy

APPLICATION OF DENSITY MATRIX THEORY TO NMR LINE-SHAPE CALCULATIONS

P. D. BUCKLEY, K. W. JOLLEY and D. N. PINDER

Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand

CONTENTS

LIST OF SYMBOLS

B_0	External magnetic field	s_x, s_y, s_z	Expectation values of the spin angular momentum in units of $h/2$
B_1	Radiofrequency magnetic field	T_2, T'_2	Transverse relaxation time in units of rad^{-1} s and Hz^{-1}, respectively
h	Planck's constant divided by 2π		
$\mathscr{H}$	Hamiltonian, or spin Hamiltonian	T_1, T'_1	Longitudinal relaxation time in units of rad^{-1} s and Hz^{-1}, respectively
$\mathscr{I}_1, \mathscr{I}_2,$	Unit matrices		
I_{xT}, I_{yT}, I_{zT}	Total angular momentum operators	Tr	Trace
I^+, I^-	Raising and lowering operators	α, β	Spin functions
		δ_{nm}	Kronecker delta
I_x, I_y, I_z	Angular momentum operators in units of $h/2$	σ	Shielding constant
		ρ	Density matrix
j	$(-1)^{\frac{1}{2}}$	ρ_{ij}	The ijth element of the density matrix
J'_{ij}	Isotropic spin–spin coupling constant between nuclei i and j in terms of linear frequency. It is related to J_{ij} by the following expression:	τ, τ'	Mean lifetime of the nucleus in a given environment in units of s rad^{-1} and Hz^{-1} respectively
	$$J'_{ij} = 2(\pi/h)J_{ij}$$	Ψ, ψ, Φ, ϕ	Wave functions
l_x, l_y, l_z	Angular momentum operators	ω_0, ω	Angular frequencies
k	Boltzmann constant	γ	Magnetogyric ratio
$\mathscr{I}, \mathscr{L}$	Operators	ω_r	γB_1
$\langle \mathscr{I} \rangle$	**Expectation value of** $\mathscr{I}$	Ω	Contraction operator
		$\otimes$	Tensor product

INTRODUCTION

Experimentally observed temperature-dependent changes in NMR spectra may be interpreted in terms of some rate process involving interchange of spins between different environments either by an intramolecular exchange process or by an intermolecular mechanism From the gross changes observed, the nucleus involved in the exchange can be identified and a mechanism by which exchange is occurring can be postulated. Depending upon the complexity of the spin system involved in the exchange process, estimates of the rate of exchange can be made by the use of approximate equations[1,2] derived from the Bloch equations.[3] These equations apply to slow, intermediate, and fast exchange situations. It has long been known, however, that these approximate treatments are quantitatively unreliable and that the most satisfactory method of determining rate constants and activation parameters is a full steady-state line-shape (the absorption mode signal as a function of frequency) fitting over the temperature range where exchange effects can be observed.[4,5]

For weakly coupled systems undergoing exchange it is possible to compute theoretical line-shapes using modified Bloch equations,[6-10] but strongly coupled systems require a full density matrix (DM) treatment.[11-12] Excellent articles are available in the literature[13-18] which describe the principles involved in DM line-shape calculations. Due in part to the economy of presentation of this method in the literature, the chemist with a less mathematical background and without specialist training in quantum mechanics may be discouraged from applying the theory to problems in which he is involved.

It is the aim of the present article to show in a practical way how to calculate line-shapes using the DM method. The article consists of three separate sections. Section A sets out in some detail, though not rigorously, the basic principles involved in DM line-shape calculations. The reader who does not have the mathematical background to follow this section can proceed directly to Section B where density matrix techniques are applied to specific NMR problems. Section C is concerned with the practical problems involved in producing theoretical spectra for exchanging systems. In sections B and C the arguments are confined to magnetic nuclei of spin $\frac{1}{2}$ only.

The article is not intended to be an extensive literature survey of the DM method in the calculation of NMR line-shapes. Where appropriate, examples will be cited from the literature but our main aim is to demonstrate the relative ease of the theoretical line-shape generation once the important equations have either been derived or simply accepted.

In this article the theory will be applied to slow passage continuous wave (CW) spectra; however, the derived line-shape equations can be applied to the frequency domain spectra obtained from pulse NMR spectrometers.

SECTION A

1. *Dirac Formulism of Quantum Mechanics*[19-24]

Introductory courses in quantum mechanics usually deal with the one-dimensional Schrödinger wave equation

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x, t)\right]\Psi(x, t) = j\hbar\frac{\partial}{\partial t}\Psi(x, t) \quad (1a)$$

or

$$\mathcal{H}\Psi(x, t) = j\hbar\frac{\partial}{\partial t}\Psi(x, t) \quad (1b)$$

and solutions for the wave function $\Psi(x, t)$ are sought. In the particular case of the potential function, $V(x, t)$, being independent of time, the wave function $\Psi(x, t)$ may be considered as a product of two functions, a spatial part, and a temporal part,

i.e. $\qquad \Psi(x, t) = \psi_n(x)\cdot\psi(t)$

where $\qquad \psi(t) = \exp(-jE_n t/\hbar)$

and $\psi_n(x)$ is an energy eigenfunction and is a solution of the energy eigen-equation,

$$\mathcal{H}\psi_n(x) = E_n\psi_n(x). \quad (2)$$

States of the quantum mechanical system in which the energy remains constant are known as stationary states.

The superposition principle infers that wave functions can be added together to form a new function which is also a physically valid representation of a possible state of the system, hence the general solution of equation (1a) is

$$\Psi(x, t) = \sum_n c_n\psi_n(x)\exp(-jE_n t/\hbar) \quad (3)$$

where the c_n's are complex numbers. The function $\Psi(x, t)$ is said to represent the state of the system in the coordinate representation and it is called the state function.

In writing equation (3) we have assumed that the $\psi_n(x)$ form a complete set of orthonormal functions,

i.e. $$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\,dx = 0, \quad m \neq n. \quad (4)$$

Provided the wave function is normalized,

$$\int_{-\infty}^{\infty} \Psi^*(x, t)\Psi(x, t)\,dx = 1 \quad (5)$$

it can be interpreted by saying that $\Psi^*(x, t)\Psi(x, t)dx$ is the probability of finding the particle in the range of values $x \rightarrow x + dx$ at time t.

Sometimes it is more convenient to have the state functions expressed as functions of momentum and time instead of position and time. Such would be the case if one were describing a wave packet. The appropriate state function, $\Phi(p, t)$, is then said to represent the system in the momentum representation.[21]

$$\Phi(p, t) = \frac{1}{\sqrt{(2\pi\hbar)}}\int_{-\infty}^{\infty} \Psi(x, t)\exp(-jpx/\hbar)\,dx.$$

Notice in this case $\Phi^*(p, t)\Phi(p, t)\mathrm{d}p$ is equal to the probability of finding the wave packet with a momentum in the range $p \rightarrow p + \mathrm{d}p$ at time t.

In fact any particular quantum mechanical system in a particular state may be described by any one of a number of different state functions each one appertaining to a different representation of the system. Each state function is a different function of a different argument thus making quantum mechanics algebraically complex.

The Dirac formulism of quantum mechanics renders the form of the analysis of any particular problem independent of the particular representation chosen. The essential feature of this formulism is the reinterpretation of equation (3). In the Dirac formulism, the orthogonal set of eigenfunctions $\psi_n(x)$ may be interpreted as unit vectors along mutually perpendicular axes in a multi-dimensional vector space. Each eigenfunction defines a direction in this space which is perpendicular to the directions defined by each of the other eigenfunctions. Hence the number of dimensions of this vector space is equal to the number of different eigenfunctions possessed by the quantum mechanical system under scrutiny. The complex numbers c_n are now to be interpreted as projections of the state vector ψ along the orthogonal set of axes. The state vector is interpreted as some kind of multi-dimensional complex vector and is given the special name "ket" and is written as $|\psi\rangle$ to indicate that it is a vectorlike quantity. Each different direction in this vector space represents a different possible state of the quantum mechanical system.

Different representations, for example, coordinate or momentum may be regarded as rotations of the coordinate *axes* in vector space, hence the ket $|\psi\rangle$ represents the state of the system no matter what representation is chosen for the analysis.

In any particular representation we may simply number the eigenkets (basis set or unit vectors) $|1\rangle$, $|2\rangle$, $|3\rangle$,... so any arbitrary ket $|\psi_a\rangle$ may be written as

$$|\psi_a\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle + \dots \quad (6a)$$

In fact the nomenclature is often further simplified by rewriting $|\psi_a\rangle$ as simply $|a\rangle$, hence (6a) becomes

$$|a\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle + \dots \quad (6b)$$

Equations (6a) and (6b) are alternative ways of writing equation (3).

As an example of the use of the Dirac formulism consider a single spin $\frac{1}{2}$ particle in a static magnetic field acting along the z-axis. The particle has two spin eigenstates; $|\alpha\rangle$ has the spin angular momentum aligned with the magnetic field and $|\beta\rangle$ has the spin angular momentum anti-aligned with the magnetic field. Hence in general the state of a spin $\frac{1}{2}$ particle may be represented by the ket $|\psi\rangle$ where

$$|\psi\rangle = c_1|\alpha\rangle + c_2|\beta\rangle.$$

The Dirac formulism of quantum mechanics must have expressions which are analogous to equations (4) and (5) which help to define a different vector-like quantity, the bra.

To each eigenket $|a\rangle$ there corresponds a different vector-like quantity, the eigenbra $\langle a|$ such that the inner (or scalar) product

$$\langle b|a\rangle = \delta_{ab} \quad (7)$$

where δ_{ab} is the Kronecker delta. These eigenbras exist in a different vector space (bra-space) which has the same dimensions as the corresponding ket-space. The eigenbras and eigenkets are in a one to one correspondence. A bra is said to be the adjoint of the corresponding ket,

i.e. $\langle a| = |a\rangle^\dagger. \quad (8)$

Also, if

$$|a\rangle = \sum_n c_n|n\rangle \quad (9)$$

then the bra corresponding to $|a\rangle$ is $\langle a|$ where

$$\begin{aligned}\langle a| = |a\rangle^\dagger &= \left[\sum_n c_n|n\rangle\right]^\dagger \\ &= \sum_n c_c^*|n\rangle^\dagger \\ &= \sum_n c_n^*\langle n| \quad (10)\end{aligned}$$

and c_n^* is the complex conjugate of c_n.

Also $\langle a|^\dagger = |a\rangle$,
$\therefore |a\rangle = |a\rangle^{\dagger\dagger}.$

Notice that taking the adjoint of a ket is rather similar to, but different from, taking the complex conjugate of a function, in that any kets involved are to be changed to bras.

The scalar product of two arbitrary state vectors is in general a complex number with the following property:

$$\langle a|b\rangle = \langle b|a\rangle^*. \quad (11)$$

This implies that the scalar product of a state vector with itself always yields a real number, the positive square root of this number is called the norm of the state vector, i.e.

$$[\langle b|b\rangle]^{\frac{1}{2}} = \text{norm } |b\rangle. \quad (12a)$$

When $|b\rangle$ is normalized its norm is unity and equation (12) becomes

$$[\langle b|b\rangle]^{\frac{1}{2}} = 1. \quad (12b)$$

2. Operators

If two kets in the same vector space are related by an expression of the form

$$|a\rangle = \mathscr{P}|b\rangle \quad (13)$$

where $\mathscr{P}$ might mean differentiation, or integration, or multiplication, etc., then $\mathscr{P}$ is said to be an operator. All operators are distinguished by the use of capital script letters, when necessary. Note that operators always act on kets from the left. Quantum mechanics, in the main, confines itself to a study of linear hermitian operators. Some of the more useful properties of linear hermitian operators are listed, together with one or two brief explanatory notes (see also subsection 4).

Since the operators are linear

$$\mathscr{P}(|a\rangle + |b\rangle) = \mathscr{P}|a\rangle + \mathscr{P}|b\rangle \qquad (14)$$

and

$$\mathscr{P}(c|b\rangle) = c(\mathscr{P}|b\rangle) \qquad (15)$$

where c is a complex number.

The sum of two operators may be defined by

$$(\mathscr{P} + \mathscr{Q})|a\rangle = \mathscr{P}|a\rangle + \mathscr{Q}|a\rangle. \qquad (16)$$

Also the product of two operators may be defined by

$$\mathscr{P}\mathscr{Q}|a\rangle = \mathscr{P}(\mathscr{Q}|a\rangle). \qquad (17)$$

The commutator of two operators is written as $[\mathscr{P}, \mathscr{Q}]$ and is defined as

$$[\mathscr{P}, \mathscr{Q}] = \mathscr{P}\mathscr{Q} - \mathscr{Q}\mathscr{P}.$$

All the above rules are satisfied by square matrices hence quantum mechanical operators may be represented as square matrices.

Operators may also act on bras so that $\langle b|$ may be transferred into $\langle a|$ by the action of some particular operator. Take the adjoint of equation (13)

$$|a\rangle\dagger = (\mathscr{P}|b\rangle)\dagger,$$

$\therefore$ using equation (8)

$$\langle a| = \langle b|\mathscr{P}\dagger. \qquad (18)$$

Notice, by convention, operators act on bras from the right. Also $\mathscr{P}\dagger$ is the adjoint of $\mathscr{P}$.

A very important example of an operator is $|n\rangle\langle m|$. This operator may act on a bra from the right to form a complex number times the bra $\langle m|$, i.e.

$$\langle b|n\rangle\langle m| = c_1\langle m| \qquad (19)$$

or $|n\rangle\langle m|$ can act on a ket from the left to form a complex number times the ket $|n\rangle$, i.e.

$$|n\rangle\langle m|b\rangle = c_2|n\rangle. \qquad (20)$$

We shall have occasion to use operators of this kind.

3. Eigenvalues and Observables

Each ket may be associated with a state of the system. There are some operators which leave the ket unchanged, e.g.

$$\mathscr{P}|b\rangle = p|b\rangle \qquad (21)$$

The ket is unchanged except for multiplication by the complex number p. It is the direction of the ket $|b\rangle$ in vector space which determines the dynamic state of the system, so under the action of the operator $\mathscr{P}$, the state of the system remains unchanged.

$|b\rangle$ is said to be an eigenket of $\mathscr{P}$ and p is the associated eigenvalue. By convention the eigenkets of an operator are written as $|p\rangle$ and the eigenvalues as p, so equation (21) becomes

$$\mathscr{P}|p\rangle = p|p\rangle. \qquad (22)$$

Furthermore, $\langle p|$ is an eigenbra of the operator $\mathscr{P}\dagger$ for taking the adjoint of (22) yields

$$\langle p|\mathscr{P}\dagger = p^*\langle p|. \qquad (23)$$

One of the postulates of quantum mechanics is that each dynamical variable of a system may be associated with a particular linear hermitian operator such that when it acts on the appropriate eigenkets the eigenvalues produced are the only possible values of the dynamical variable which may be obtained by measurement. Hence equation (21) may be reinterpreted as follows. A measurement of the dynamical variable represented by $\mathscr{P}$ always yields the value p, when the quantum mechanical system is in the eigenstate $|p\rangle$. No matter how many times the measurement is made the same value p is always obtained.

If the system is not in an eigenstate of $\mathscr{P}$ but is in some arbitrary state $|\psi\rangle$, then we can use equation (6) to write

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle + \ldots$$

where the kets on the right are eigenkets of $\mathscr{P}$

$$\therefore \mathscr{P}|\psi\rangle = c_1p_1|1\rangle + c_2p_2|2\rangle + c_3p_3|3\rangle + \ldots \qquad (24)$$

But the only possible results of the measurement are p_1, p_2, p_3, etc., so equation (24) has to be carefully interpreted. The very act of measurement must force the quantum mechanical system to jump into one of its eigenstates (in equation (24) one of the coefficients, c, goes to unity, the others to zero). This renders equation (24) an eigenequation. The probability of obtaining the value p_1 by measurement is $c_1^2/\sum_n c_n^2$ and the probability of obtaining the value p_2 is $c_2^2/\sum_n c_n^2$, etc.

If we have an ensemble of identical quantum mechanical systems all prepared in exactly the same way, and hence all in the same arbitrary state $|\psi\rangle$, then we may define the expectation value of any dynamical quantity as the average value of p obtained by making precisely the same measurement once on each system in turn. This ensemble average value of p, $\langle\mathscr{P}\rangle$ is clearly given by

$$\langle\mathscr{P}\rangle = \frac{c_1^2}{\sum_n c_n^2}p_1 + \frac{c_2^2}{\sum_n c_n^2}p_2 + \cdots + \frac{c_n^2 p_n}{\sum_n c_n^2}\cdots \qquad (25a)$$

which may also be written,

$$\langle\mathscr{P}\rangle = \frac{\langle\psi|\mathscr{P}\psi\rangle}{\langle\psi|\psi\rangle}. \qquad (25b)$$

Equation (25b) can be shown to be identical with equation (25a) by substituting expressions for $\langle\psi|$ and $|\psi\rangle$ from equations (9) and (10) and recognizing that, since $|p\rangle$ is an eigenket, $\langle n|m\rangle = \delta_{nm}$ (see equation (7)) and $\mathscr{P}|n\rangle = p_n|n\rangle$.

Notice the vertical bar of the ket in the numerator has been omitted to indicate that $\mathscr{P}$ acts on the ket. When $|\psi\rangle$ is normalized we may use equation (12b) in (25b) to obtain

$$\langle\mathscr{P}\rangle = \langle\psi|\mathscr{P}\psi\rangle. \qquad (25c)$$

It should be noted that a single measurement cannot yield $\langle\mathscr{P}\rangle$, it is an *ensemble* average with each member of the ensemble in the same initial state.

4. Hermitian Operators

In general the eigenvalues of linear operators are complex numbers, but dynamical variables such as

position, momentum, or energy always yield real numbers when they are measured. So only those operators which have real eigenvalues may be associated with dynamical variables, such operators are called hermitian operators. [This does not mean that linear operators with complex eigenvalues are not useful in quantum mechanics, on the contrary, the annihilation and creation operators, sometimes called the lowering and raising operators, play an important role in quantum mechanics in such diverse fields as quantum optics and NMR.] A necessary and sufficient condition for the eigenvalues of an operator to be real is that the operator must be equal to its own adjoint, i.e.

$$\mathscr{P} = \mathscr{P}\dagger.$$

This self-adjoint property of hermitian operators may be demonstrated as follows: Multiply equation (22) from the left by $\langle p|$ to obtain

$$\langle p|\mathscr{P}p\rangle = p\langle p|p\rangle. \tag{26}$$

Similarly multiply equation (23) from the right with $|p\rangle$ to obtain

$$\langle p\mathscr{P}\dagger|p\rangle = p^*\langle p|p\rangle. \tag{27}$$

If p is real then the left-hand sides of equations (26) and (27) are equal

$$\therefore \langle p\mathscr{P}\dagger|p\rangle = \langle p|\mathscr{P}p\rangle \tag{28}$$

indicating that $\mathscr{P} = \mathscr{P}\dagger$.

The hermitian property of an operator is usually indicated by writing equation (28) as

$$\langle p|\mathscr{P}|p\rangle = p \tag{29}$$

where it is assumed that $|p\rangle$ is normalized.

The expectation value for an hermitian operator becomes from equations (25c), (28) and (29)

$$\langle \mathscr{P} \rangle = \langle \psi|\mathscr{P}|\psi \rangle. \tag{30}$$

5. *Matrix Operators*

All dynamical variables may be associated with linear hermitian operators. These operators obey a set of algebraic laws which are the same as the laws of matrix algebra, hence the operators of quantum mechanics may be represented by square hermitian matrices. This presentation of quantum mechanics is called matrix mechanics and is the presentation used in the major part of this article.

Matrix mechanics requires kets to be represented by column matrices and bras by row matrices. This can be illustrated by considering the inner (or scalar) product of a ket with its corresponding bra. This was previously defined as $\langle \psi|\psi \rangle$. Hence, using equations (6) and (10)

$$\langle \psi|\psi \rangle = |c_1|^2 + |c_2|^2 + |c_3|^2 + \ldots \tag{31}$$

This result may be obtained by considering $\langle \psi|$ to be the row matrix

$$[c_1^* \; c_2^* \; c_3^* \ldots]$$

and $|\psi\rangle$ to be the column matrix

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \cdot \\ \cdot \end{bmatrix}$$

i.e.
$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle + \ldots$$

$$\equiv \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \cdot \\ \cdot \end{bmatrix} \tag{32}$$

and
$$\langle \psi| = c_1^*\langle 1| + c_2^*\langle 2| + c_3^*\langle 3| + \ldots$$

$$\equiv [c_1^* \; c_2^* \; c_3^* \; \ldots], \tag{33}$$

$$\therefore \langle \psi|\psi \rangle = [c_1^* c_2^* c_3^* \ldots] \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ \cdot \end{bmatrix}$$

$$= |c_1|^2 + |c_2|^2 + |c_3|^2 + \ldots \tag{34}$$

which is identical to equation (31).

Examples of the representation of operators as matrices

Consider the two-dimensional vector space with orthogonal eigenkets $|1\rangle$ and $|2\rangle$.

(a) Let an arbitrary ket $|b\rangle$ be given by $|b\rangle = c_1|1\rangle + c_2|2\rangle$

i.e.
$$|b\rangle = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

Let the matrix operator $\mathscr{P}$ act on $|b\rangle$ and transform it into the ket $|a\rangle$

If

$$\mathscr{P} = \begin{bmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{bmatrix} \tag{35}$$

then

$$|a\rangle = \mathscr{P}|b\rangle$$

becomes

$$|a\rangle = \begin{bmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$\therefore |a\rangle = \begin{bmatrix} p_{11}c_1 + p_{12}c_2 \\ p_{21}c_1 + p_{22}c_2 \end{bmatrix}$$

i.e. $|a\rangle = (p_{11}c_1 + p_{12}c_2)|1\rangle + (p_{21}c_1 + p_{22}c_2)|2\rangle.$ (36)

(b) If the quantum mechanical system is initially in the state $|b\rangle$ then the expectation value of $\mathscr{P}$, $\langle \mathscr{P} \rangle$, is

given by

$$\langle \mathscr{P} \rangle = \langle b | \mathscr{P} | b \rangle \quad \text{(see equation (30))}.$$

Now

$$\mathscr{P}|b\rangle = \begin{bmatrix} p_{11}c_1 + p_{12}c_2 \\ p_{21}c_1 + p_{22}c_2 \end{bmatrix}$$

$$\therefore \langle \mathscr{P} \rangle = \begin{bmatrix} c_1^* & c_2^* \end{bmatrix} \begin{bmatrix} p_{11}c_1 + p_{12}c_2 \\ p_{21}c_1 + p_{22}c_2 \end{bmatrix}$$

i.e. $\quad \langle \mathscr{P} \rangle = p_{11}c_1c_1^* + p_{12}c_2c_1^* + p_{21}c_1c_2^* + p_{22}c_2c_2^*.$

$$(37)$$

However, if the eigenvalues of $\mathscr{P}$ are real numbers, then $\langle b|\mathscr{P}|b\rangle = (\langle b|\mathscr{P}|b\rangle)^*$, so equation (37) must be equal to its own complex conjugate. This is only true in general if $p_{12}^* = p_{21}$, $p_{11}^* = p_{11}$, and $p_{22}^* = p_{22}$. That is the matrix elements must be related by

$$p_{ij}^* = p_{ji}. \qquad (38)$$

Matrices with this property are called self-hermitian adjoint. All matrix operators which represent dynamical variables possess this property. Notice the hermitian adjoint of a matrix is formed by interchanging rows and columns and taking the complex conjugate.

(c) The ket $|b\rangle$ is given by

$$|b\rangle = c_1|1\rangle + c_2|2\rangle$$

$$= \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}.$$

Therefore the eigenket $|1\rangle$ is given by

$$|1\rangle = 1|1\rangle + 0|2\rangle$$

$$= \begin{bmatrix} 1 \\ 0 \end{bmatrix}.$$

Similarly the eigenket $|2\rangle$ is given by

$$|2\rangle = 0|1\rangle + 1|2\rangle$$

$$= \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

(d) In general the matrix element p_{ij} is given by

$$p_{ij} = \langle i|\mathscr{P}|j\rangle \qquad (39)$$

where $\langle i|$ is an eigenbra and $|j\rangle$ is an eigenket,

e.g. $\quad \langle 1|\mathscr{P}|2\rangle = \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

$$= p_{12}.$$

6. The Trace

Equation (37) is an expression for the expectation value of an operator in a two-dimensional vector space, i.e.

$$\langle \mathscr{P} \rangle = \langle b|\mathscr{P}|b\rangle = p_{11}c_1c_1^* + p_{12}c_2c_1^* + p_{21}c_1c_2^* + p_{22}c_2c_2^*. \qquad (40)$$

We may consider the complex number products $c_ic_j^*$ to define a matrix with elements c_{ij}. Therefore (37) may be rewritten as

$$\langle \mathscr{P} \rangle = p_{11}c_{11} + p_{12}c_{21} + p_{21}c_{12} + p_{22}c_{22}. \qquad (41)$$

Consider the matrix product $\mathscr{P}\mathscr{C}$

$$= \begin{bmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{bmatrix} \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix}$$

$$= \begin{bmatrix} p_{11}c_{11} + p_{12}c_{21} & p_{11}c_{12} + p_{12}c_{22} \\ p_{21}c_{11} + p_{22}c_{21} & p_{21}c_{12} + p_{22}c_{22} \end{bmatrix}$$

By inspection the left-hand side of equation (41) is given by the sum of the diagonal terms of the matrix product $\mathscr{P}\mathscr{C}$. This sum is called the trace of $\mathscr{P}\mathscr{C}$ and is written as Tr $\mathscr{P}\mathscr{C}$.

Therefore

$$\langle \mathscr{P} \rangle = \text{Tr } \mathscr{P}\mathscr{C}$$

$$= \text{Tr } \mathscr{C}\mathscr{P}. \qquad (42)$$

The expectation value is amenable to measurement, therefore it must be independent of the set of eigenkets used as the basis set for the expansion of $|b\rangle$. So the trace too must be independent of the basis set chosen for the expansion of $|b\rangle$. Consequently one is free to choose the most convenient set of kets to act as the basis set. This point will be illustrated later in the analysis of the coupled spin $\frac{1}{2}$ systems.

7. Angular Momentum Operators

One of the problems of quantum mechanics is the construction of linear hermitian operators which may represent the dynamical variables of the quantum mechanical system under study. When the dynamical variable has a classical analogue the relevant operator may be readily identified; however, when the dynamical variable is essentially quantum mechanical and has no classical counterpart, the identification of the appropriate linear hermitian operator may present some difficulties.

The intrinsic spin of an elementary particle is a dynamic variable which does not have a classical counterpart and consequently the identification of square hermitian matrix operators which may represent spin is not obvious. However, one can obtain the form of the angular momentum matrix operators.[21]

Classically the total angular momentum, $\tilde{l}$, of a particle about some arbitrary point is a vector quantity given by

$$\tilde{l} = \tilde{u} \times \tilde{p} \qquad (43)$$

where $\tilde{u}$ is the position vector of the particle from the point and $\tilde{p}$ is the momentum of the particle. Hence, for example, the angular momentum about the x-axis is

$$l_x = yp_z - zp_y.$$

Also the total angular momentum is related to the component values by the relationship

$$l^2 = l_x^2 + l_y^2 + l_z^2. \qquad (44)$$

The operator form of the Heisenberg Uncertainty Principle is

$$q_rp_s - p_sq_r = j\hbar\delta_{rs} \qquad (45)$$

where r and s may represent any of the cartesian coordinates x, y, or z; p_r, and q_r are the operators representing the r component of momentum and displacement respectively. Equation (45) is the commutation relationship governing the position and momentum operators. If the commutator of two operators is non-zero then no ket may be simultaneously an eigenket of both these operators.

Using equations (43), (44) and (45) we can readily deduce the commutation relations that govern the angular momentum operators, viz.

$$[l_r, l_s] = jhl_t \qquad (46)$$

where r, s and t form a cyclic permutation, and l_r is the operator representing the component of angular momentum about the r-axis,

e.g.

$$[l_x, l_y] = jhl_z$$

or

$$l_x l_y - l_y l_x = jhl_z.$$

Also

$$[l_r, l^2] = 0. \qquad (47)$$

The commutation relationships of equations (46) and (47) determine the properties of the angular momentum operators,[24,25] including by hypothesis, spin angular momentum which has no classical counterpart. Confining our attention to spin angular momentum, equation (47) implies that a ket may be an eigenket of l^2 and l_z, say. This means that we can choose a basis set such that the matrix operators representing l^2 and l_z are both diagonal but the other spin angular momentum operators are non-diagonal.

Considering spin $\frac{1}{2}$ particles spectroscopic evidence suggests that the eigenvalues of l^2 are $\frac{1}{2}(1 + \frac{1}{2})h^2$ and those of l_z are $+\frac{1}{2}h$ and $-\frac{1}{2}h$. This implies that the matrix representations of l^2 may be written as

$$l^2 = \tfrac{3}{4}h^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

and the matrix representation of l_z may be written as:

$$l_z = \frac{h}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

Hence, using equations (46) and (47) we find:

$$l_x = \frac{h}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

and

$$l_y = \frac{h}{2} \begin{bmatrix} 0 & -j \\ j & 0 \end{bmatrix}.$$

Thus the matrix operators which represent a spin $\frac{1}{2}$ particle in the representation that renders l_z diagonal are:

$$l_z = \frac{h}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = hI_z,$$

$$l_y = j\frac{h}{2} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} = hI_y.$$

$$l_x = \frac{h}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = hI_x.$$

$$l^2 = \tfrac{3}{4}h^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = h^2 I. \qquad (48)$$

The eigenket which yields the eigenvalue $+h/2$ for the projection of the spin angular momentum along the z-direction is $|1\rangle$ where

$$|1\rangle = |\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad (49a)$$

(spin up case), i.e.

$$\frac{h}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{h}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix}.$$

Similarly the eigenket which yields the eigenvalue $-h/2$ for the projection of the spin angular momentum along the z-direction is $|2\rangle$ where

$$|2\rangle = |\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \qquad (49b)$$

(spin down case), i.e.

$$\frac{h}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = -\frac{h}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

Notice that the kets are in a two-dimensional space, as expected, since I_z has two non-degenerate eigenvalues (see subsection 1).

The spin matrix operators for a spin 1 particle in the representation which renders I_z diagonal may be obtained in a similar manner. The results are as follows:

$$l_x = \frac{h}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$l_y = j\frac{h}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \qquad (50)$$

$$l_z = h \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

The corresponding eigenkets for l_z are

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

$$|2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \qquad (51)$$

$$|3\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

8. The Tensor Product[24]

Consider a quantum mechanical system consisting of one spin $\frac{1}{2}$ particle *and* one spin 1 particle. The projection of the total spin angular momentum along the z-axis is given by

$$l_{zT} = l_{z1} + l_{z2} \qquad (52)$$

where l_{z1}, and l_{z2} are the projections of the spin angular momenta of the individual particles along the z-axis.

Also

$$l_{z1} = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

and

$$l_{z2} = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\therefore l_{zT} = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

But this last matrix addition is not defined so the simplistic argument given above must be invalid.

The matrix operator l_{z1}, is defined in a two-dimensional vector space appertaining to the spin $\frac{1}{2}$ particle, *vector space 1*. The matrix operator l_{z2} is defined in a three-dimensional vector space associated with the spin 1 particle, *vector space 2*. The quantum mechanical system which consists of both particles requires a composite vector space which combined both component vector spaces, *vector space 3*. This composite space is called "product space". Operators appertaining to the composite quantum mechanical system may be constructed from the operators which appertain to each component particle of the system by the application of the tensor product.

To form a matrix operator for vector space *3* we must couple together vector spaces *1* and *2* and add the contributions from each particle. The component vector spaces may be coupled together through tensor multiplication by the appropriate unit matrices.

The tensor product of a 2 × 2 matrix and a 3 × 3 matrix is defined as

Notice the tensor product of a 2 × 2 matrix with a 3 × 3 matrix is a 6 × 6 matrix. The tensor product is indicated by the symbol ⊗.

The correct expression for l_{zT} is

$$l_{zT} = (l_{z1} \otimes \mathscr{I}_2) + (\mathscr{I}_1 \otimes l_{z2}) \qquad (54)$$

where $\mathscr{I}_1$ and $\mathscr{I}_2$ are the unit matrices of vector spaces *1* and *2* respectively.

Equation (54) may be considered as the coupling together of the component vector spaces and then the addition of the contribution of each particle.

$$l_{z1} \otimes \mathscr{I}_2 = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \frac{\hbar}{2}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\mathscr{I}_1 \otimes l_{z2} = \hbar \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$= \hbar \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

i.e.

$$l_{zT} = \hbar \begin{bmatrix} \frac{3}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{3}{2} \end{bmatrix} \qquad (55)$$

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \otimes \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} = \begin{bmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{11}b_{13} & a_{12}b_{11} & a_{12}b_{12} & a_{12}b_{13} \\ a_{11}b_{21} & a_{11}b_{22} & a_{11}b_{23} & a_{12}b_{21} & a_{12}b_{22} & a_{12}b_{23} \\ a_{11}b_{31} & a_{11}b_{32} & a_{11}b_{33} & a_{12}b_{31} & a_{12}b_{32} & a_{12}b_{33} \\ a_{21}b_{11} & a_{21}b_{12} & a_{21}b_{13} & a_{22}b_{11} & a_{22}b_{12} & a_{22}b_{13} \\ a_{21}b_{21} & a_{21}b_{22} & a_{21}b_{23} & a_{22}b_{21} & a_{22}b_{22} & a_{22}b_{23} \\ a_{21}b_{31} & a_{21}b_{32} & a_{21}b_{33} & a_{22}b_{31} & a_{22}b_{32} & a_{22}b_{33} \end{bmatrix} \qquad (53)$$

This may be written in a shorthand form as

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \otimes \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} = \begin{bmatrix} a_{11}[b] & a_{12}[b] \\ a_{21}[b] & a_{22}[b] \end{bmatrix}$$

The eigenkets for the composite system may also be obtained from the component "eigenkets" by application of the tensor product. The component "eigenkets" are given in equations (49) and (51).

Eigenvalues of l_{zT}

$$|1_T\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad 3\hbar/2$$

$$|2_T\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad \tfrac{1}{2}\hbar$$

$$|3_T\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad -\tfrac{1}{2}\hbar$$

$$|4_T\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \qquad \tfrac{1}{2}\hbar$$

$$|5_T\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} \qquad -\tfrac{1}{2}\hbar$$

$$|6_T\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \qquad -3\hbar/2.$$

Notice $|1_T\rangle$ is an eigenket of l_{zT} the eigenvalue being $3\hbar/2$, etc.

9. The Density Matrix[26,27]

In subsection 4 we obtained an expression for the expectation value of a dynamical variable when the state of the quantum mechanical system could be described by a single ket $|\psi\rangle$. A system can only be described by a single ket if we have as much knowledge of the system as is permitted by quantum mechanics, the system is then said to be in a *pure state*.

Consider a quantum mechanical system whose state cannot be described by a single ket because we have insufficient knowledge of the system. The system is said to be in a *mixed state* and it is best described by stating the probability q_ψ of the system being in the state $|\psi\rangle$.

In this case the expectation value of any operator may be obtained from a generalization of equation (37).

$$\langle \mathscr{P} \rangle = \sum_\psi q_\psi \langle \mathscr{P}_\psi \rangle = \sum_\psi q_\psi \langle \psi | \mathscr{P} | \psi \rangle \qquad (56)$$

where $\sum_\psi q_\psi = 1$ because the q_ψ's are probabilities.

Equation (56) implies that we construct an ensemble with quantum mechanical systems in various states $|\psi\rangle$ weighted according to their probabilities q_ψ. The expectation value is therefore a kind of double ensemble average; once over the possible eigenvalues of $\mathscr{P}$, and once over the weighted possible states of the system. The first average is a typical quantum mechanical average and is represented by the angled brackets, the second is a typical statistical average and is represented by the bar.

Using equation (6) we may express $|\psi\rangle$ as a series of eigenkets

$$|\psi\rangle = \sum_r c_{\psi r} |r\rangle. \qquad (57)$$

Therefore the expectation value for an ensemble of systems all in the same state $|\psi\rangle$ is given by

$$\langle \mathscr{P}_\psi \rangle = \sum_r \sum_s c_{\psi r}^* c_{\psi s} \langle r | \mathscr{P} | s \rangle$$

where equations (37), (10), and (6) have been used. Therefore, using equation (56), we obtain an expression for the expectation value of an ensemble of systems in a mixed state.

$$\langle \mathscr{P} \rangle = \sum_\psi \sum_r \sum_s q_\psi c_{\psi r}^* c_{\psi s} \langle r | \mathscr{P} | s \rangle$$

$$= \sum_r \sum_s \left(\sum_\psi q_\psi c_{\psi rs} \right) p_{rs}$$

where $c_{\psi r}^* c_{\psi s}$ has been identified as the element $c_{\psi rs}$ of some square matrix C, and equation (39) has been used to identify the matrix element p_{rs} of the matrix operator $\mathscr{P}$.

Let

$$\sum_\psi q_\psi c_{\psi rs} = \bar{\rho}_{sr}. \qquad (58)$$

Therefore equation (56) may be rewritten as

$$\langle \mathscr{P} \rangle = \sum_\psi q_\psi \langle \mathscr{P}_\psi \rangle = \sum_r \sum_s \bar{\rho}_{sr} p_{rs}$$

and by comparison with equation (41)

$$\langle \mathscr{P} \rangle = \mathrm{Tr}\bar{\rho}\mathscr{P} = \mathrm{Tr}\mathscr{P}\bar{\rho}. \qquad (59)$$

$\bar{\rho}$ is called the density matrix operator, its great significance is illustrated in equation (59) in that it enables the easy computation of the expectation values of observables. When the density matrix is employed in describing an ensemble of similar systems equation (58) may be rewritten as

$$\bar{\rho}_{rs} = \frac{1}{N} \sum_{n=1}^{N} c_{nsr} \qquad (60)$$

where N is the total number of systems present, and $c_{n\sigma}$ is the appropriate element of the density matrix of the nth system.

It is clear from equations (57) and (58) that the elements of the density matrix depend upon the particular representation used, that is on the set of eigenkets used as the basis set. However, the expectation value of the operator $\mathscr{P}$ obviously does not depend upon the choice of basis set. Therefore $\mathrm{Tr}\,\bar{\rho}\mathscr{P}$ is independent of the choice of basis set even though $\bar{\rho}$ is dependent on that choice.

The srth element of the density matrix operator is defined by equation (58) to be

$$\begin{aligned}\bar{\rho}_{sr} &= \sum_{\psi} q_{\psi} c_{\psi rs} \\ &= \sum_{\psi} q_{\psi} c^{*}_{\psi r} c_{\psi s} \\ &= \sum_{\psi} q_{\psi}\langle s|\psi\rangle\langle\psi|r\rangle \\ &= \sum_{\psi} \langle s|\psi\rangle q_{\psi}\langle\psi|r\rangle \end{aligned} \qquad (61)$$

But, from equation (39).

$$\bar{\rho}_{sr} = \langle s|\bar{\rho}|r\rangle$$

therefore

$$\bar{\rho} = \sum_{\psi} |\psi\rangle q_{\psi}\langle\psi|. \qquad (62)$$

10. *Properties of the Density Matrix Operators*

(a) $\mathrm{Tr}\,\bar{\rho} = 1$,

i.e. $\quad \mathrm{Tr}\left(\sum_{\psi}|\psi\rangle q_{\psi}\langle\psi|\right) = \mathrm{Tr}\sum_{\psi} q_{\psi}\langle\psi|\psi\rangle = 1.$

(b) $\bar{\rho}$ is hermitian,

i.e. $\quad \bar{\rho}^{\dagger} = \left(\sum_{\psi}|\psi\rangle q_{\psi}\langle\psi|\right)^{\dagger} = \sum_{\psi}|\psi\rangle q_{\psi}\langle\psi| = \bar{\rho}.$

(c) $\bar{\rho}$ is positive definite.

The elements of the principal diagonal are probabilities and so are real and positive, and, since $\mathrm{Tr}\,\bar{\rho} = 1$, each of these elements must lie between zero and unity. It may be shown that any positive definite hermitian operator of unit trace may be considered as a density operator in some representation or other.

(d) For a pure state

$$\mathrm{Tr}\,(\bar{\rho})^{2} = 1. \qquad (63)$$

A pure state implies that one of the q_{ψ}'s is unity and all the others are zero.

Therefore

$$\bar{\rho} = |\psi\rangle\langle\psi| \qquad (64)$$

and

$$\begin{aligned}(\bar{\rho})^{2} &= |\psi\rangle\langle\psi|\psi\rangle\langle\psi| \\ &= \bar{\rho}.\end{aligned}$$

Since

$$\mathrm{Tr}\,\bar{\rho} = 1,$$
$$\mathrm{Tr}\,(\bar{\rho})^{2} = 1.$$

(e) The density matrix evolves in time according to the "equation of motion".

$$j\hbar\frac{\mathrm{d}\bar{\rho}}{\mathrm{d}t} = \mathscr{H}\bar{\rho} - \bar{\rho}\mathscr{H} = [\mathscr{H}, \bar{\rho}]. \qquad (65)$$

11. *The Application of the Density Operators to an Ensemble of Spin $\frac{1}{2}$ Particles*

From equation (59) the expectation values of the projections of the spin angular momentum along the spatial axes x, y and z are

$$\langle l_{x}\rangle = \mathrm{Tr}\,\bar{\rho}l_{x} = \frac{\hbar}{2}\bar{s}_{x},$$

$$\langle l_{y}\rangle = \mathrm{Tr}\,\bar{\rho}l_{y} = \frac{\hbar}{2}\bar{s}_{y},$$

$$\langle l_{z}\rangle = \mathrm{Tr}\,\bar{\rho}l_{z} = \frac{\hbar}{2}\bar{s}_{z} \qquad (66)$$

where $\bar{s}_{x}$, $\bar{s}_{y}$ and $\bar{s}_{z}$ are the expectation values of the appropriate projections of the spin angular momentum in units of $\hbar/2$. We have chosen the representation that renders l_{z} diagonal, the spin operators for each particle are thus the 2×2 matrix operators given by equation (48). Hence $\bar{\rho}$ is also a 2×2 matrix operator. The basis set of kets chosen are the eigenkets of l_{z} given by equation (49).

If for any particular particle the expectation values of all the spin projections are known, then the state of the particle is pure and the ket may be written as $|\psi\rangle = c_{1}|1\rangle + c_{2}|2\rangle$. Moreover, since the particle is in a pure state, $\rho = |\psi\rangle\langle\psi|$ and we may use equation (39) to obtain the elements of the density matrix as illustrated below.

$$\rho_{11} = \langle 1|\rho|1\rangle = \langle 1|\psi\rangle\langle\psi|1\rangle = c_{1}c^{*}_{1}$$
$$\rho_{12} = \langle 1|\rho|2\rangle = \langle 1|\psi\rangle\langle\psi|2\rangle = c_{1}c^{*}_{2},$$

i.e.

$$\rho = \begin{bmatrix} |c_{1}|^{2} & c_{1}c^{*}_{2} \\ c_{2}c^{*}_{1} & |c_{2}|^{2} \end{bmatrix}$$

The density matrix elements can be determined in terms of s_{x}, s_{y} and s_{z} from the relationships

$$\rho_{11} + \rho_{22} = 1,$$

$$\mathrm{Tr}\,\rho l_{z} = \frac{\hbar}{2}(\rho_{11} - \rho_{22}) = \frac{\hbar}{2}s_{z},$$

$$\mathrm{Tr}\,\rho l_{x} = \frac{\hbar}{2}(\rho_{12} + \rho_{21}) = \frac{\hbar}{2}s_{x},$$

$$\mathrm{Tr}\,\rho l_{y} = \frac{\hbar}{2}j(\rho_{12} - \rho_{21}) = \frac{\hbar}{2}s_{y}.$$

Therefore

$$\rho = \frac{1}{2}\begin{bmatrix} 1 + s_{z} & s_{x} - js_{y} \\ s_{x} + js_{y} & 1 - s_{z} \end{bmatrix}$$

Hence, if the state of the particle is known, then the expectation values of the projections of the spin angular momentum are known and consequently the elements of the density matrix are known.

Clearly the ensemble density matrix is

$$\bar{\rho} = \tfrac{1}{2}\begin{bmatrix} 1 + \bar{s}_z & \bar{s}_x - j\bar{s}_y \\ \bar{s}_x + j\bar{s}_y & 1 - \bar{s}_z \end{bmatrix}$$

where $\bar{s}_x$, $\bar{s}_y$ and $\bar{s}_z$ are the appropriate ensemble averages of s_x, s_y and s_z.

Notice that $\mathrm{Tr}\,\bar{\rho}$ is still unity but

$$\mathrm{Tr}(\bar{\rho})^2 = \tfrac{1}{2}(1 + \bar{s}_x^2 + \bar{s}_y^2 + \bar{s}_z^2)$$
$$= \tfrac{1}{2}(1 + |\bar{s}|^2).$$

An ensemble in a pure state has each particle with its spin aligned in the same direction (the particles are said to be completely polarized). In this case $|\bar{s}| = 1$ and hence $\mathrm{Tr}(\bar{\rho})^2 = 1$.

In general the particles of the ensemble are not completely polarized and $|\bar{s}| < 1$ and $\mathrm{Tr}(\bar{\rho})^2 < 1$. For a completely random ensemble $|\bar{s}| = 0$ and $\mathrm{Tr}(\bar{\rho})^2 = \tfrac{1}{2}$.

Examples

(i)
$$\bar{\rho} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$$

$\mathrm{Tr}\,\bar{\rho} = 1$, and $\mathrm{Tr}(\bar{\rho})^2 = 1$,

∴ the ensemble is in a pure state.

Also $\mathrm{Tr}\,\bar{\rho}l_z = \hbar/2$ therefore each particle is aligned with "spin up", all particles are in the eigen state $|\alpha\rangle$ of the operator l_z.

(ii)
$$\bar{\rho} = \begin{bmatrix} \tfrac{1}{2} & 0 \\ 0 & \tfrac{1}{2} \end{bmatrix}$$

$\mathrm{Tr}\,\bar{\rho} = 1$, but $\mathrm{Tr}(\bar{\rho})^2 = \tfrac{1}{2}$.

Also $\mathrm{Tr}\,\bar{\rho}l_z = 0$. The ensemble is not in a pure state, there are equal numbers of particles in the eigenstates $|\alpha\rangle$, and $|\beta\rangle$ of the operator l_z.

(iii)
$$\bar{\rho} = \begin{bmatrix} \tfrac{1}{2} & \tfrac{1}{2} \\ \tfrac{1}{2} & \tfrac{1}{2} \end{bmatrix}$$

$\mathrm{Tr}\,\bar{\rho} = 1$, $\mathrm{Tr}(\bar{\rho})^2 = 1$

The ensemble is in a pure state.
Also $\mathrm{Tr}\,\bar{\rho}l_z = 0$, $\mathrm{Tr}\,\bar{\rho}l_x = \hbar/2$, $\mathrm{Tr}\,\bar{\rho}l_y = 0$.

The fact that $\langle l_z \rangle$ is zero indicates that there are equal numbers of particles in the eigenstates $|\alpha\rangle$, and $|\beta\rangle$ of the operator l_z.

In each case considered the basis set used is formed from the eigenkets of the operator l_z, and moreover, in each case ρ_{11} is proportional to the probability of finding the system in the eigenket $|\alpha\rangle$ and ρ_{22} is proportional to the probability of finding the system in the eigenket $|\beta\rangle$.

This is a general result, the density matrix elements along the principal diagonal are proportional to the probability of finding a particle in the corresponding eigenket.

12. *Ensemble of Particles in Thermal Equilibrium*

Consider an ensemble of identical weakly interacting particles in thermal equilibrium, the available energy levels being labelled E_i. From classical statisti-

cal mechanics, the probability of finding a particle in the E_ith energy level is

$$p_i = \frac{\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}. \tag{67}$$

In the representation in which the energy matrix operator is diagonal the density operator may be written as

$$\bar{\rho}^0 = \frac{\exp(-\mathscr{H}/kT)}{\mathrm{Tr}\,\exp(-\mathscr{H}/kT)} \tag{68}$$

where $\exp(-\mathscr{H}/kT)$ is understood to imply[28,29]

$$\mathscr{I} - \frac{\mathscr{H}}{kT} + \frac{1}{2}\frac{\mathscr{H}\mathscr{H}}{k^2 T^2} + \cdots \tag{69}$$

$\mathscr{H}$, the Hamiltonian operator, is defined in equation (1).

1. *The Spin Hamiltonian of the Multi-spin $\tfrac{1}{2}$ System*[24]

Consider an ensemble of identical molecules each having a single spin $\tfrac{1}{2}$ nucleus as the only magnetic nucleus. When this ensemble is subjected to a large stationary magnetic field B_0 acting in the $-z$ direction, the spin Hamiltonian for each magnetic nucleus may be written as

$$\mathscr{H} = (1 - \sigma)\hbar\gamma B_0 I_z \tag{70}$$

where γ is the magnetogyric ratio and I_z is defined in equation (48). This Hamiltonian represents the quantum mechanical equivalent of the potential energy $(-\tilde{\mu} \cdot \tilde{B}_0)$ of a classical bar magnet of magnetic moment $\tilde{\mu}$ immersed in a magnetic field $\tilde{B}_0$. This illustrates nicely the (essentially quantum mechanical) relationship between the magnetic moment of a nucleus and its spin angular momentum. This concept will be alluded to below when we indicate that the magnitude of the magnetization of a sample is directly proportional to the net spin angular momentum of the sample.

By considering the spin Hamiltonian separately we are assuming that the spin state of the nucleus is independent of the electronic, rotational, vibrational, etc., states of the whole molecule. This is certainly not so. We even make some attempt to weaken this assumption by introducing the factor σ, the so-called shielding constant which is due to the shielding effect of the electron orbitals about and near the nucleus. The shielding effect should be taken into account by introducing a tensor quantity, $\tilde{\sigma}$, but for fluid samples the molecules suffer many collisions during the lifetime of excited nuclear states, so the molecules tumble and the shielding effect may be represented by the scalar quantity $\sigma(=\tfrac{1}{3}\mathrm{Tr}\,\tilde{\sigma})$.[30]

Assuming no spin–spin coupling, the Hamiltonian of a molecule containing two or more magnetic nuclei is

$$\mathscr{H} = \sum_{i=1}^{n} \omega_{0i}\hbar I_{zi}, \qquad \omega_{0i} = (1 - \sigma_i)\gamma B_0 \text{ rad s}^{-1} \tag{71}$$

where the subscript i describes the environment of the ith magnetic nucleus. However, some form of spin–spin coupling is usually present, for magnetic nucleus n effects the electron orbitals about itself which in turn effect the electron orbitals about magnetic nucleus $n + 1$, and so on. This interaction between the two magnetic nuclei m and n may be represented as a scalar product

$$V_{nm} = \hbar^2 J'_{nm} I_n \cdot I_m \qquad (72)$$

where $\hbar I$ is the appropriate total spin operator and J' is the coupling constant. The coupling constant J which is measured in a NMR experiment is in hertz and is related to J' by the relationship

$$J = \frac{\hbar J'}{2\pi}.$$

The scalar product may be expanded as

$$I_n \cdot I_m = I_{zn} I_{zm} + \tfrac{1}{2}(I_n^+ I_m^- + I_n^- I_m^+)$$

where

$$I_n^+ = I_{xn} + j I_{yn} \text{ and } I_n^- = I_{xn} - j I_{yn}.$$

For a molecule containing many magnetic nuclei the total spin–spin coupling energy is obtained by summing over all pairs of magnetic nuclei

$$V = \sum_{n<m} \sum \hbar^2 J'_{nm} I_n \cdot I_m. \qquad (73)$$

The NMR spectrum is probed by applying a small amplitude radio-frequency magnetic field $2B_1 \cos \omega t$ along the x-axis thereby making the total Hamiltonian

$$\mathcal{H} = \sum_i \hbar \gamma_i B_0 (1 - \sigma_i) I_{zi} - \hbar \gamma_i 2 B_1 I_{xi} \cos \omega t$$
$$+ \sum_{n<m} \sum \hbar^2 J'_{nm} I_n \cdot I_m \qquad (74)$$

where the matrix representations of I_x and I_z are given in equation (48). (This means that we have chosen the basis set of kets to render I_z diagonal.)

The linearly polarized magnetic field $2B_1 \cos \omega t$ may be resolved into a pair of circularly polarized fields with equal amplitudes rotating in opposite directions in the x-y plane.
Algebraically

$$(2B_1 \cos \omega t)\tilde{e}_x = B_1(\tilde{e}_x \cos \omega t - \tilde{e}_y \sin \omega t)$$
$$+ B_1(\tilde{e}_x \cos \omega t + \tilde{e}_y \sin \omega t)$$

where $\tilde{e}_x$ and $\tilde{e}_y$ are unit vectors in the x and y directions, respectively. Only one of these rotating magnetic field components has the same sense as the Larmor precession of the nuclear magnetic moment about B_0. And, provided that $B_1 \ll B_0$, the circularly polarized field whose sense is opposite to that of the Larmor precession produces insignificant changes in the orientation of the magnetic moment of the spin $\tfrac{1}{2}$ nucleus. Hence the out-of-phase component can be neglected and we need only consider the in-phase component of the applied radio-frequency magnetic field. This field contributes to the energy of the magnetic nu-

clei and so it too makes a contribution to the spin Hamiltonian. We obtain simpler algebraic expressions for the Hamiltonian if we abandon the laboratory reference frame and instead consider a set of cartesian axes which rotate about the z-axis in such a sense that the applied radio-frequency field appears to remain fixed in magnitude and directed along the x-axis of the rotating axes. The Hamiltonian for the molecule in the rotating reference frame is,

$$\mathcal{H} = -\omega \hbar \sum_i I_{zi} + \hbar \sum_i \omega_{0i} I_{zi} + \hbar \gamma B_1 \sum_i I_{xi}$$
$$+ \hbar^2 \sum_{n<m} \sum J'_{nm} I_n \cdot I_m. \qquad (75)$$

This expression for $\mathcal{H}$ may be substituted into equation (65) and, making use of the selection rules (this is discussed in subsection 3, this section), it may be shown that the component form of the equation of motion of the density matrix is

$$\frac{d\rho_{kl}}{dt} = -j\rho_{kl}\left\{\sum_i (\omega_{0i} - \omega)[(I_{zi})_{kk} - (I_{zi})_{ll}]\right.$$
$$\left. + \hbar \sum_{i<j} J'_{ij}[(I_{zi} I_{zj})_{kk} - (I_{zi} I_{zj})_{ll}]\right\}$$
$$+ \frac{j}{2} \hbar \sum_{i<j} J'_{ij}[\rho,(I_i^+ I_j^- + I_i^- I_j^+)]_{kl}$$
$$+ j\gamma B_1(\rho_{kk} - \rho_{ll}) \sum_i (I_{xi})_{kl}. \qquad (76)$$

It should be noted that equation (76) takes no account of the relaxation of nuclear spins.

We recall the paragraph just after equation (70) and observe that the NMR absorption-mode spectrum line shape is proportional to the expectation value of the magnetization in the y direction and hence $\langle I_y \rangle$

$$\left\langle \sum_n I_{yn} \right\rangle = \langle I_{yT} \rangle = \text{Tr}(\rho I_{yT}) \qquad (77)$$

The required density matrix elements can be obtained by solving equation (76).

The treatment of the "rotating-axes" aspects of this subsection has been of a pseudo-classical nature.[31]

2. Derivation of the Bloch Equations

The solution of a particular problem using the density matrix method will illustrate the application of the essential equations that have been derived in Section A. As in the derivation of the Bloch equations set out here, the calculation of line-shapes involves the correct use of a limited number of equations.

We consider an ensemble of molecules each of which contain one spin $\tfrac{1}{2}$ nucleus as its only effective magnetic nucleus. Hence there is no spin–spin coupling term and the Hamiltonian of equation (74) reduces to[24]

$$\mathcal{H} = -\omega_0 \hbar I_z - \hbar \gamma B_1 \cos \omega t I_x + \hbar \gamma B_1 \sin \omega t I_y$$

Note that in this subsection B_0 is defined in the $+z$ direction so that the Bloch equations are obtained in their usual form.

Substituting for I_x, I_y and I_z from equation (48),

$$\mathscr{H} = -\omega_0 \hbar \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} - \hbar \gamma B_1 \cos \omega t \begin{bmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{bmatrix}$$

$$+ \hbar \gamma B_1 \sin \omega t \begin{bmatrix} 0 & -\dfrac{j}{2} \\ \dfrac{j}{2} & 0 \end{bmatrix} \quad (78)$$

$$\therefore \mathscr{H} = \hbar \begin{bmatrix} -\omega_0/2 & -\dfrac{\gamma B_1}{2} e^{j\omega t} \\ -\dfrac{\gamma B_1}{2} e^{-j\omega t} & \dfrac{\omega_0}{2} \end{bmatrix}$$

The density matrix for an ensemble of spin $\frac{1}{2}$ nuclei may be written as

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}$$

where, for convenience, the bar above the density matrix has been omitted, although its presence throughout the remainder of the article is to be understood.

The time derivative of the density matrix is given by equation (65). If this equation is divided through by $\hbar$ we obtain

$$j \frac{d\rho}{dt} = \mathscr{H} \rho - \rho \mathscr{H} \quad (79)$$

where $\mathscr{H}$ as now written differs from the $\mathscr{H}$ of equation (78) by the factor $\hbar$, so $\mathscr{H}$ is now expressed in rad s^{-1} instead of joules. It is also necessary to introduce phenomenological terms describing the relaxation of the density matrix elements towards their equilibrium values in the absence of the applied radio-frequency magnetic field. In terms of the basis set of functions chosen, both the Hamiltonian matrix and the density matrix would be diagonal in the absence of the applied radio-frequency magnetic field. So if this radio-frequency field were suddenly reduced to zero the off-diagonal density matrix elements would decay to zero with a time constant of, say, T_2. The diagonal density matrix elements would decay to the new equilibrium values with a time constant of T_1. The relaxation to equilibrium of the off-diagonal elements is due to interactions between the spin $\frac{1}{2}$ nuclei and the rest of the system, whereas the decay of the diagonal density matrix elements necessarily involves transitions between states.

Including relaxation effects equation (79) can be written as

$$\frac{d\rho}{dt} = \frac{1}{j} (\mathscr{H} \rho - \rho \mathscr{H})$$

$$+ \frac{(\rho^0_{\text{diagonal}} - \rho_{\text{diagonal}})}{T_1} - \frac{\rho_{\text{off-diagonal}}}{T_2} \quad (80)$$

where the thermal equilibrium density matrix ρ^0 is given by equation (68)

$$\rho^0 = \exp(-\mathscr{H}/kT)/\text{Tr} \exp(-\mathscr{H}/kT).$$

The subscript "diagonal" indicates that only the diagonal elements are to be included, similarly the subscript "off-diagonal" indicates that only the off-diagonal elements are to be included.

Equating matrix elements equation (80) becomes

$$j\dot{\rho}_{11} = \frac{\gamma B_1}{2} (\rho_{12} e^{-j\omega t} - \rho_{21} e^{j\omega t}) - jT_1^{-1}(\rho_{11} - \rho^0_{11}),$$

$$j\dot{\rho}_{12} = -\omega_0 \rho_{12} + \frac{\gamma B_1}{2} e^{j\omega t}(\rho_{11} - \rho_{22}) - jT_2^{-1}\rho_{12},$$

$$j\dot{\rho}_{21} = \omega_0 \rho_{21} - \frac{\gamma B_1}{2} e^{-j\omega t}(\rho_{11} - \rho_{22}) - jT_2^{-1}\rho_{21},$$

$$j\dot{\rho}_{22} = \frac{\gamma B_1}{2} (\rho_{21} e^{j\omega t} - \rho_{12} e^{-j\omega t}) - jT_1^{-1}(\rho_{22} - \rho^0_{22}).$$

$$(81)$$

These equations may be regarded as a set of simultaneous equations with the density matrix elements as unknowns. As indicated in subsection 1 (this section), the observable quantities are the magnetization of the sample in the x, y and z directions. These quantities are proportional to the expectation values of the operators representing the projections of the angular momentum along the x, y and z directions respectively.

$$\langle M_x \rangle \alpha \langle I_x \rangle,$$
$$\langle M_y \rangle \alpha \langle I_y \rangle,$$
$$\langle M_z \rangle \alpha \langle I_z \rangle.$$

Therefore, using equation (59),

$$\langle M_x \rangle = C \, \text{Tr} \, \rho I_x,$$
$$\langle M_y \rangle = C \, \text{Tr} \, \rho I_y,$$
$$\langle M_z \rangle = C \, \text{Tr} \, \rho I_z.$$

where C is a proportionality constant.
Now

$$\rho I_x = \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{bmatrix} = \begin{bmatrix} \dfrac{\rho_{12}}{2} & \dfrac{\rho_{11}}{2} \\ \dfrac{\rho_{22}}{2} & \dfrac{\rho_{21}}{2} \end{bmatrix}$$

$$\therefore \text{Tr} \, \rho I_x = \tfrac{1}{2}(\rho_{12} + \rho_{21}) = \frac{\langle M_x \rangle}{C}.$$

Similarly

$$\text{Tr} \, \rho I_y = j\tfrac{1}{2}(\rho_{12} - \rho_{21}) = \frac{\langle M_y \rangle}{C},$$

$$\text{Tr} \, \rho I_z = \tfrac{1}{2}(\rho_{11} - \rho_{22}) = \frac{\langle M_z \rangle}{C}.$$

$$\left. \right\} \quad (82)$$

Differentiating equation (82) with respect to time and substituting for, first the time dependence of the density matrix elements from equation (81), and then

expressions for the density matrix elements in terms of $\langle M_x \rangle$, $\langle M_y \rangle$ and $\langle M_z \rangle$ from equation (82), we obtain

$$
\left.
\begin{aligned}
\langle \dot{M}_y \rangle &= -\omega_0 \langle M_x \rangle + \gamma B_1 \cos \omega t \langle M_z \rangle \\
&\quad - \langle M_y \rangle / T_2, \\
\langle \dot{M}_x \rangle &= \omega_0 \langle M_y \rangle + \gamma B_1 \sin \omega t \langle M_z \rangle \\
&\quad - \langle M_x \rangle / T_2, \\
\langle \dot{M}_z \rangle &= -\gamma B_1 \cos \omega t \langle M_y \rangle \\
&\quad - \gamma B_1 \sin \omega t \langle M_x \rangle \\
&\quad - (\langle M_z \rangle - \langle M_z^0 \rangle) / T_1.
\end{aligned}
\right\}
\tag{83}
$$

These are the Bloch equations.

3. Intramolecular Exchange

In order to study the effects of intramolecular exchange we must include in equation (80) the effects of exchange of magnetic nuclei between different environments in the same molecule. If magnetic nuclei exchange environments then the initial spin ket of the molecule $|\psi\rangle$ is changed to $\mathscr{R}|\psi\rangle$, where $\mathscr{R}$ is called the exchange operator. Also as will be illustrated below $\mathscr{R}^2 = 1$. Hence, using the definition of ρ given in equation (64), on exchange ρ is transformed to $\mathscr{R}\rho\mathscr{R}$. If τ is the mean lifetime of the nucleus in each environment then the rate of change of ρ due to exchange is $(\mathscr{R}\rho\mathscr{R} - \rho)/\tau$. Therefore the effects of intramolecular exchange may be included in equation (80) by the addition of this term.

Thus the equation of motion of the density matrix including the radio-frequency probing field and the effects of intramolecular exchange is

$$
\frac{d\rho}{dt} = \frac{\mathscr{R}\rho\mathscr{R} - \rho}{\tau} + j[\rho, \mathscr{H}]
$$

$$
+ \frac{\rho^0_{\text{diagonal}} - \rho_{\text{diagonal}}}{T_1} - \frac{\rho^0_{\text{off-diagonal}}}{T_2}. \tag{84}
$$

Notice that $\mathscr{H}$ is expressed in rad s^{-1}. This equation may be written in component form as[5] (see equation (76))

$$
\frac{d\rho_{kl}}{dt} = \frac{1}{\tau}\left[\sum_{n,m} \mathscr{R}_{kn}\rho_{nm}\mathscr{R}_{ml} - \rho_{kl} \right] - \rho_{kl}/T_2
$$

$$
- j\rho_{kl}\left\{ \sum_i (\omega_{0i} - \omega)[(I_{zi})_{kk} - (I_{zi})_{ll}] \right.
$$

$$
\left. + \hbar \sum_{i<j} J'_{ij}[(I_{zi}I_{zj})_{kk} - (I_{zi}I_{zj})_{ll}] \right\}
$$

$$
+ \frac{j}{2}\hbar \sum_{i<j} J'_{ij}[\rho,(I_i^+ I_j^- + I_i^- I_j^+)]_{kl}
$$

$$
+ j\omega_r(\rho_{kk} - \rho_{ll}) \sum_i (I_{xi})_{kl} \tag{85a}
$$

where ω is the angular frequency of the applied r.f. field and $\omega_r = \gamma B_1$. Fortunately there are some simplifications which are usually applied to these equations. Firstly, the NMR experiment is normally performed under "slow-passage" conditions, and hence we may

set the right-hand sides of equations (84) and (85a) to zero. Secondly, the radio-frequency field B_1 is negligible compared with the stationary field B_0, consequently the significant transitions are governed by the usual selection rule $\Delta m_z = \pm 1$. This means that those density matrix elements linking energy levels between forbidden radiative transitions may be neglected. Finally we simplify the last term (the driving term) in equation (85a). The diagonal elements of the density matrix are proportional to the probability of finding a molecule of the system in the appropriate energy level, for example ρ_{33} is proportional to the probability of finding a molecule in the third energy level. The differences between the energy levels in the NMR experiment are so small compared with the Boltzmann energy, kT, that the differences between the diagonal elements of the density matrix may all be set equal to the product of a constant and Δm_z. The driving term is the only term in equation (85a) that includes B_1 so adjusting the constant in this term merely alters the vertical scale of the theoretical spectrum.

Using the slow-passage approximation equation (85a) can be written in terms of linear frequency:

$$
0 = \left(\sum_{n,m} \mathscr{R}_{kn}\rho_{nm}\mathscr{R}_{ml} - \rho_{kl} \right)/\tau' - \rho_{kl}/T_2'
$$

$$
- j\rho_{kl}\left\{ \sum_i (\nu_{0i} - \nu)[(I_{zi})_{kk} - (I_{zi})_{ll}] \right\}
$$

$$
- j\rho_{kl} \sum_{i<j} J_{ij}[(I_{zi}I_{zj})_{kk} - (I_{zi}I_{zj})_{ll}]
$$

$$
+ (j/2) \sum_{i<j} J_{ij}[\rho,(I_i^+ I_j^- + I_j^+ I_i^-)]_{kl}
$$

$$
+ j\nu_r(\rho_{kk} - \rho_{ll}) \sum_i (I_{xi})_{kl} \tag{85b}
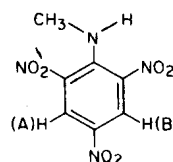$$

where

$$
\frac{1}{\tau'} = \frac{1}{2\pi\tau}, \quad \frac{1}{T_2'} = \frac{1}{2\pi T_2},
$$

$$
\nu = \frac{\omega}{2\pi} \quad \text{and} \quad J_{ij} = \frac{\hbar J'_{ij}}{2\pi}.
$$

AB Spin System Undergoing Internal Rotation

Consider the internal rotation of part of a molecule which contains two spin $\frac{1}{2}$ nuclei such as the picryl protons of N-methyl-2,4,6-trinitro aniline[32].

In the slow-exchange limit these protons make up an AB quartet. The protons exchange their environment by rotating about the C—N(H)(CH₃) bond. We choose as our basis set the simple product-kets formed from

α and β defined in subsection 7, Section A. Hence the basis set is

$$|\psi_1\rangle = \alpha\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad m_z = 1$$

$$|\psi_2\rangle = \alpha\beta = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \quad m_z = 0$$

$$|\psi_3\rangle = \beta\alpha = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \quad m_z = 0$$

$$|\psi_4\rangle = \beta\beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \quad m_z = -1$$

where nucleus A is written first, and the magnetic quantum number is given on the right. Under exchange conditions nucleus A exchanges magnetic environment with nucleus B. Prior to rotation the basis set is formed by writing nucleus A first, after rotation the basis set is formed by writing nucleus B first.

	Before rotation	After rotation
(i)	$\|\psi_1\rangle = \alpha\alpha$	$\alpha\alpha = \|\psi_1\rangle$
(ii)	$\|\psi_2\rangle = \alpha\beta$	$\beta\alpha = \|\psi_3\rangle$
(iii)	$\|\psi_3\rangle = \beta\alpha$	$\alpha\beta = \|\psi_2\rangle$
(iv)	$\|\psi_4\rangle = \beta\beta$	$\beta\beta = \|\psi_4\rangle$

Making use of the exchange operator $\mathscr{R}$ defined earlier in this section the rotation can be represented in matrix notation as,

(i) $\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$ becomes $\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$ i.e. $\mathscr{R}\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$ $\therefore R_{11} = 1$

(ii) $\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}$ becomes $\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$ i.e. $\mathscr{R}\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$ $\therefore R_{32} = 1$

(iii) $\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$ becomes $\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}$ i.e. $\mathscr{R}\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}$ $\therefore R_{23} = 1$

(iv) $\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$ becomes $\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$ i.e. $\mathscr{R}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$ $\therefore R_{44} = 1$

In this case the exchange operator $\mathscr{R}$ is a 4×4 matrix, its only non-zero elements being listed above on the right.

$$\mathscr{R} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Notice how easy it is to identify the elements of the transformation matrix when we know the initial and final forms of the molecular spin kets. Dirac[19] presents a general method for identifying the elements of the transformation matrix.

If nucleus A exchanges with B, and then B exchanges with A, the net result is that A and B regain their initial magnetic environments, mathematically

$$|\psi\rangle = \mathscr{R}\mathscr{R}|\psi\rangle$$
$$= \mathscr{R}^2|\psi\rangle.$$
$$\therefore \mathscr{R}^2 = I.$$

The pre-exchange density matrix, ρ, becomes $\mathscr{R}\rho\mathscr{R}$ on exchange where,

$$\mathscr{R}\rho\mathscr{R} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} \\ \rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} \\ \rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} \\ \rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{13} & \rho_{12} & \rho_{14} \\ \rho_{31} & \rho_{33} & \rho_{32} & \rho_{34} \\ \rho_{21} & \rho_{23} & \rho_{22} & \rho_{24} \\ \rho_{41} & \rho_{43} & \rho_{42} & \rho_{44} \end{bmatrix}$$

Therefore on exchange ρ_{12} becomes ρ_{13}, ρ_{42} becomes ρ_{43} and so on.

The Hamiltonian for the two spin $\frac{1}{2}$ system undergoing intramolecular exchange reduces to

$$\mathscr{H} = -\omega(I_{zA} + I_{zB}) + \omega_{0A}I_{zA} + \omega_{0B}I_{zB}$$
$$+ \omega_r(I_{xA} + I_{xB}) + J'_{AB}\hbar I_{zA}I_{zB}$$
$$+ \tfrac{1}{2}J'_{AB}\hbar(I_A^+ I_B^- + I_A^- I_B^+) \qquad (86a)$$

where $\mathscr{H}$ is in rad s^{-1} (see equation (75)). However $\mathscr{H}$ is usually written in terms of linear frequency, viz.

$$\mathscr{H} = -\nu(I_{zA} + I_{zB}) + \nu_{0A}I_{zA} + \nu_{0B}I_{zB}$$
$$+ \nu_r(I_{xA} + I_{xB}) + J_{AB}I_{zA}I_{zB}$$
$$+ \tfrac{1}{2}J_{AB}(I_A^+ I_B^- + I_A^- I_B^+) \qquad (86b)$$

where $\omega = 2\pi\nu$ and $J_{AB} = \hbar J'_{AB}/2\pi$.

$\mathcal{H}$ as now written differs from that of equation (86a) by a factor of $1/2\pi$. Substituting values of I_{zA}, I_{yA}, etc., as defined in equation (48) we obtain the following matrix representations for the terms in equation (86b):

$$I_{zA} = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix}$$

$$I_{zB} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix}$$

$$I_{zA}I_{zB} = \begin{bmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 \\ 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{bmatrix}$$

$$I_A^+ I_B^- + I_A^- I_B^+ = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

and so on. Therefore the matrix representation of the Hamiltonian given in equation (86b) is

$$\mathcal{H} = \begin{bmatrix} \Delta v + J/4 & v_r/2 & v_r/2 & 0 \\ v_r/2 & \delta v - J/4 & J/2 & v_r/2 \\ v_r/2 & J/2 & -\delta v - J/4 & v_r/2 \\ 0 & v_r/2 & v_r/2 & -\Delta v + J/4 \end{bmatrix}$$

$$(87)$$

where $J = J_{AB}$, $\Delta v = \frac{1}{2}(v_{0A} + v_{0B}) - v$, and $\delta v = \frac{1}{2}(v_{0A} - v_{0B})$. From equation (77) the NMR spectrum line shape is proportional to

to give the following equations:

$$j\left[(\rho_{11} - \rho_{22})\frac{v_r}{2} + \left(\delta v - \frac{J}{4}\right)\rho_{12} + \frac{J}{2}\rho_{13}\right.$$
$$\left. - \left(\Delta v + \frac{J}{4}\right)\rho_{12}\right] - \frac{\rho_{12}}{T_2'}$$
$$+ \frac{\rho_{13} - \rho_{12}}{\tau'} = 0,$$

$$j\left[(\rho_{11} - \rho_{33})\frac{v_r}{2} + \left(-\delta v - \frac{J}{4}\right)\rho_{13} + \frac{J}{2}\rho_{12}\right.$$
$$\left. - \left(\Delta v + \frac{J}{4}\right)\rho_{13}\right] - \frac{\rho_{13}}{T_2'}$$
$$+ \frac{\rho_{12} - \rho_{13}}{\tau'} = 0,$$

$$j\left[(\rho_{22} - \rho_{44})\frac{v_r}{2} - \left(\delta v - \frac{J}{4}\right)\rho_{24} - \frac{J}{2}\rho_{34}\right.$$
$$\left. + \left(-\Delta v + \frac{J}{4}\right)\rho_{24}\right] - \frac{\rho_{24}}{T_2'}$$
$$+ \frac{\rho_{34} - \rho_{24}}{\tau'} = 0,$$

$$j\left[(\rho_{33} - \rho_{44})\frac{v_r}{2} + \left(\delta v + \frac{J}{4}\right)\rho_{34} - \frac{J}{2}\rho_{24}\right.$$
$$\left. + \left(-\Delta v + \frac{J}{4}\right)\rho_{34}\right] - \frac{\rho_{34}}{T_2'}$$
$$+ \frac{\rho_{24} - \rho_{34}}{\tau'} = 0. \qquad (88b)$$

These equations can be solved to obtain the required density matrix elements. Substitution of these elements into equation (88a) gives $\langle I_{yT} \rangle$. A graph of $\langle I_{yT} \rangle$ against v is the observed "absorption mode" NMR spectrum. This particular example is worked out in full in Section C.

$$\langle I_{yT} \rangle = \text{Tr}\,\rho I_{yT}$$

$$I_{yT} = \sum_{i=1}^{2} I_{yi} = \begin{bmatrix} 0 & -\frac{j}{2} \\ \frac{j}{2} & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & -\frac{j}{2} \\ \frac{j}{2} & 0 \end{bmatrix} = \frac{j}{2}\begin{bmatrix} 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \end{bmatrix}$$

$$\therefore \text{Tr}\,\rho I_{yT} = \frac{1}{2}j(\rho_{12} + \rho_{13} + \rho_{24} + \rho_{34} - \rho_{21} - \rho_{31} - \rho_{42} - \rho_{43})$$
$$= \text{Im}(\rho_{21} + \rho_{31} + \rho_{42} + \rho_{43})$$

since ρ is hermitian,

$$\text{Tr}\,\rho I_{yT} = -\text{Im}(\rho_{12} + \rho_{13} + \rho_{24} + \rho_{34}). \qquad (88a)$$

The sign is irrelevant since $\rho_{ll} - \rho_{kk}$ will be set arbitrarily.

The Hamiltonian matrix of equation (87) may now be used in equation (84), and the simplifications described in the paragraph after equation (85a) made,

Multi-spin System Undergoing Internal Rotation

The mathematical manipulations required to obtain the line-shape function are really no more complicated in multi-spin cases than they are in the two spin $\frac{1}{2}$ case.