COMPLEMENTS OF CHAPTER IV

A_{IV} : THE PAULI MATRICES B_{IV} : DIAGONALIZATION OF A 2 × 2 HERMITIAN MATRIX	A_{IV}, B_{IV} : technical study of 2 × 2 matrices; simple, and important for solving numerous quantum mechanical problems.
C_{IV}: FICTITIOUS SPIN 1/2 ASSOCIATED WITH A TWO-LEVEL SYSTEM	C_{IV}: establishes the close relation which exists between §§ B and C of chapter IV; supplies a simple geometrical interpretation of the properties of two-level systems (easy, but not indispensable for what follows).
D_{IV}: SYSTEM OF TWO SPIN 1/2 PARTICLES	D_{IV}: simple illustration of the tensor product and the postulates of quantum mechanics (can be considered to be a set of worked exercises).
E_{IV}: SPIN 1/2 DENSITY MATRIX	E_{IV}: illustration, in the case of spin 1/2 particles, of concepts introduced in complement E_{III}.
F_{IV}: SPIN 1/2 PARTICLE IN A STATIC MAGNETIC FIELD AND A ROTATING FIELD : MAGNETIC RESONANCE	F_{IV}: study of a very important physical phenomenon with many applications: magnetic resonance; can be studied later.
G_{IV}: A SIMPLE MODEL OF THE AMMONIA MOLECULE	G_{IV}: example of a physical system whose study can be reduced, in a first approximation, to that of a two-level system; moderately difficult.
H_{IV}: COUPLING BETWEEN A STABLE STATE AND AN UNSTABLE STATE	H_{IV}: study of the influence of coupling between two levels with different lifetimes; easy, but requires the concepts introduced in complement K_{III}.
J_{IV}: EXERCISES	

Complement A_{IV}

THE PAULI MATRICES

1. Definition; eigenvalues and eigenvectors
2. Simple properties
3. A convenient basis of the 2 × 2 matrix space

In § A-2 of chapter IV, we introduced the matrices which represent the three components S_x, S_y and S_z of a spin **S** in the $\{ | + \rangle, | - \rangle \}$ basis (eigenvectors of S_z). In quantum mechanics, it is often convenient to introduce the dimensionless operator $\boldsymbol{\sigma}$, proportional to **S** and given by:

$$\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma} \tag{1}$$

The matrices which represent the three components of $\boldsymbol{\sigma}$ in the $\{ | + \rangle, | - \rangle \}$ basis are called the "Pauli matrices".

1. Definition ; eigenvalues and eigenvectors

Let us go back to equations (A-15), (A-16) and (A-17) of chapter IV. Using (1), we see that the definition of the Pauli matrices is:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2}$$

These are Hermitian matrices, all three of which have the same characteristic equation:

$$\lambda^2 - 1 = 0 \tag{3}$$

The eigenvalues of σ_x, σ_y and σ_z are therefore:

$$\lambda = \pm 1 \tag{4}$$

which is consistent with the fact that those of S_x, S_y and S_z are $\pm \hbar/2$.

It is easy to obtain, from definition (2), the eigenvectors of σ_x, σ_y and σ_z. They are the same, respectively, as those of S_x, S_y and S_z, already introduced in § A-2 of chapter IV:

$$\begin{aligned} \sigma_x | \pm \rangle_x &= \pm | \pm \rangle_x \\ \sigma_y | \pm \rangle_y &= \pm | \pm \rangle_y \\ \sigma_z | \pm \rangle &= \pm | \pm \rangle \end{aligned} \tag{5}$$

with:

$$|\pm\rangle_x = \frac{1}{\sqrt{2}}[|+\rangle \pm |-\rangle]$$

$$|\pm\rangle_y = \frac{1}{\sqrt{2}}[|+\rangle \pm i|-\rangle] \tag{6}$$

2. Simple properties

It is easy to see from definition (2) that the Pauli matrices verify the relations:

$$\text{Det}\,(\sigma_j) = -1 \qquad j = x, y \quad \text{or} \quad z \tag{7}$$

$$\text{Tr}\,(\sigma_j) = 0 \tag{8}$$

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I \qquad \text{(where } I \text{ is the } 2 \times 2 \text{ unit matrix)} \tag{9}$$

$$\sigma_x\sigma_y = -\sigma_y\sigma_x = i\sigma_z \tag{10}$$

as well as the equations which can be deduced from (10) by cyclic permutation of x, y and z.

Equations (9) and (10) are sometimes condensed into the form:

$$\sigma_j\,\sigma_k = i\sum_l \varepsilon_{jkl}\,\sigma_l + \delta_{jk}\,I \tag{11}$$

where ε_{jkl} is antisymmetric with respect to the interchange of any two of its indices. It is equal to:

$$\varepsilon_{jkl} = \begin{cases} 0 \text{ if the indices } j, k, l \text{ are not all different} \\ 1 \text{ if } j, k, l \text{ is an even permutation of } x, y, z \\ -1 \text{ if } j, k, l \text{ is an odd permutation of } x, y, z \end{cases} \tag{12}$$

From (10), we immediately conclude:

$$[\sigma_x, \sigma_y] = 2i\sigma_z \tag{13}$$

(and the relations obtained by cyclic permutation). This yields:

$$\begin{aligned} [S_x, S_y] &= i\hbar S_z \\ [S_y, S_z] &= i\hbar S_x \\ [S_z, S_x] &= i\hbar S_y \end{aligned} \tag{14}$$

We shall see later (*cf.* chap. VI) that equations (14) are characteristic of an angular momentum.

We also see from (10) that:

$$\sigma_x\sigma_y + \sigma_y\sigma_x = 0 \tag{15}$$

(the σ_i matrices are said to anticommute with each other) and that, taking (9) into account:

$$\sigma_x\sigma_y\sigma_z = iI \tag{16}$$

Finally, let us mention an identity which is sometimes useful in quantum mechanics. If **A** and **B** denote two vectors whose components are numbers (or operators which commute with all operators acting in the two-dimensional spin state space):

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B}\, I + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \tag{17}$$

We see that, using formula (11) and the fact that **A** and **B** commute with $\boldsymbol{\sigma}$, we can write:

$$\begin{aligned}(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= \sum_{j,k} \sigma_j A_j \sigma_k B_k \\ &= \sum_{j,k} A_j B_k \left[i \sum_l \varepsilon_{jkl} \sigma_l + \delta_{jk} I \right] \\ &= i \sum_l \sigma_l \left[\sum_{j,k} \varepsilon_{jkl} A_j B_k \right] + \sum_j A_j B_j I \end{aligned} \tag{18}$$

In the second term, we recognize the scalar product **A** . **B**. In addition, it is easy to see from (12) that $\sum_{j,k} \varepsilon_{jkl} A_j B_k$ is the lth component of the vector product **A** × **B**. This proves (17). Note that if **A** and **B** do not commute, they must appear in the same order on both sides of the identity.

3. A convenient basis of the 2 × 2 matrix space

Consider an arbitrary 2 × 2 matrix:

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \tag{19}$$

It can always be written as a linear combination of the four matrices:

$$I,\ \sigma_x,\ \sigma_y,\ \sigma_z \tag{20}$$

since, using (2), we can immediately verify that:

$$M = \frac{m_{11} + m_{22}}{2} I + \frac{m_{11} - m_{22}}{2} \sigma_z + \frac{m_{12} + m_{21}}{2} \sigma_x + i \frac{m_{12} - m_{21}}{2} \sigma_y \tag{21}$$

Therefore, any 2 × 2 matrix can be put in the form:

$$M = a_0 I + \mathbf{a} \cdot \boldsymbol{\sigma} \tag{22}$$

where the coefficients a_0, a_x, a_y and a_z are complex numbers.

Comparing (21) and (22), we see that M is Hermitian if and only if the coefficients a_0 and **a** are real. These coefficients can be expressed formally in terms of the matrix M in the following manner:

$$a_0 = \frac{1}{2} \mathrm{Tr}\,(M) \tag{23-a}$$

$$\mathbf{a} = \frac{1}{2} \mathrm{Tr}\,(M\boldsymbol{\sigma}) \tag{23-b}$$

These formulas can easily be proven from (8), (9) and (10).

Complement B_{IV}
DIAGONALIZATION OF A 2 × 2 HERMITIAN MATRIX

1. Introduction

In quantum mechanics, one must often diagonalize 2 × 2 matrices. When we need only the eigenvalues, it is very easy to solve the characteristic equation since it is of second degree. In principle, the calculation of the normalized eigenvectors is also extremely simple; however, if it is performed clumsily, it can lead to expressions which are unnecessarily complicated and difficult to handle.

The goal of this complement is to present a simple method of calculation which is applicable in all cases. After having changed the origin of the eigenvalues, we introduce the angles θ and φ, defined in terms of the matrix elements, which enable us to write the normalized eigenvectors in a simple easy-to-use form. The angles θ and φ also have an interesting physical interpretation in the study of two-level systems, as we shall see in complement C_{IV}.

2. Changing the eigenvalue origin

Consider the Hermitian matrix:

$$(H) = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{1}$$

H_{11} and H_{22} are real. Moreover:

$$H_{12} = H_{21}^* \tag{2}$$

The matrix (H) therefore represents, in an orthonormal basis, $\{ |\varphi_1\rangle, |\varphi_2\rangle \}$, a certain Hermitian operator H*.

* We use the letter H because the Hermitian operator which we are trying to diagonalize is often a Hamiltonian. Nevertheless, the calculations presented in this complement can obviously be applied to any 2 × 2 Hermitian matrix.

Using the half-sum and half-difference of the diagonal elements H_{11} and H_{22}, we can write (H) in the following way:

$$(H) = \begin{pmatrix} \frac{1}{2}(H_{11}+H_{22}) & 0 \\ 0 & \frac{1}{2}(H_{11}+H_{22}) \end{pmatrix} + \begin{pmatrix} \frac{1}{2}(H_{11}-H_{22}) & H_{12} \\ H_{21} & -\frac{1}{2}(H_{11}-H_{22}) \end{pmatrix} \quad (3)$$

It follows that the operator H itself can be decomposed into:

$$H = \frac{1}{2}(H_{11}+H_{22})\,\mathbb{1} + \frac{1}{2}(H_{11}-H_{22})\,K \quad (4)$$

where $\mathbb{1}$ is the identity operator and K is the Hermitian operator represented in the $\{ |\varphi_1\rangle, |\varphi_2\rangle \}$ basis by the matrix:

$$(K) = \begin{pmatrix} 1 & \frac{2H_{12}}{H_{11}-H_{22}} \\ \frac{2H_{21}}{H_{11}-H_{22}} & -1 \end{pmatrix} \quad (5)$$

It is clear from (4) hat H and K have the same eigenvectors. Let $|\psi_\pm\rangle$ be these eigenvectors, and $E_\pm$ and $\kappa_\pm$, the corresponding eigenvalues for H and K:

$$H|\psi_\pm\rangle = E_\pm|\psi_\pm\rangle \quad (6)$$

$$K|\psi_\pm\rangle = \kappa_\pm|\psi_\pm\rangle \quad (7)$$

From (4), we immediately conclude that:

$$E_\pm = \frac{1}{2}(H_{11}+H_{22}) + \frac{1}{2}(H_{11}-H_{22})\,\kappa_\pm \quad (8)$$

Finally, the first matrix appearing on the right-hand side of (3) plays a minor role: we could make it disappear by choosing for the eigenvalue origin $(H_{11}+H_{22})/2$★.

3. Calculation of the eigenvalues and eigenvectors

a. ANGLES θ AND φ

Let θ and φ be the angles defined in terms of the matrix elements H_{ij} by:

$$\tan\theta = \frac{2|H_{21}|}{H_{11}-H_{22}} \qquad \text{with } 0 \leqslant \theta < \pi \quad (9)$$

$$H_{21} = |H_{21}|\,e^{i\varphi} \qquad \text{with } 0 \leqslant \varphi < 2\pi \quad (10)$$

★ Furthermore, this new origin is the same, whatever the basis $\{ |\varphi_1\rangle, |\varphi_2\rangle \}$ initially chosen, since $H_{11}+H_{22} = \mathrm{Tr}(H)$ is invariant under a change of orthonormal bases.

φ is the argument of the complex number H_{21}. According to (2), we have $|H_{12}| = |H_{21}|$ and:

$$H_{12} = |H_{12}|\, e^{-i\varphi} \tag{11}$$

If we use (9), (10) and (11), the matrix (K) becomes:

$$(K) = \begin{pmatrix} 1 & \tan\theta\, e^{-i\varphi} \\ \tan\theta\, e^{i\varphi} & -1 \end{pmatrix} \tag{12}$$

b. EIGENVALUES OF K

The characteristic equation of the matrix (12)

$$\text{Det}\,[(K) - \kappa I] = \kappa^2 - 1 - \tan^2\theta = 0 \tag{13}$$

directly yields the eigenvalues κ_+ and κ_- of (K):

$$\kappa_+ = +\frac{1}{\cos\theta} \tag{14-a}$$

$$\kappa_- = -\frac{1}{\cos\theta} \tag{14-b}$$

We see that they are indeed real (property of a Hermitian matrix, *cf.* § D-2-a of chapter II). If we want to express $1/\cos\theta$ in terms of H_{ij}, all we need to do is use (9) and notice that $\cos\theta$ and $\tan\theta$ have the same sign since $0 \leqslant \theta < \pi$:

$$\frac{1}{\cos\theta} = \frac{\sqrt{(H_{11}-H_{22})^2 + 4\,|H_{12}|^2}}{H_{11}-H_{22}} \tag{15}$$

c. EIGENVALUES OF H

Using (8), (14) and (15), we immediately obtain:

$$E_+ = \frac{1}{2}(H_{11}+H_{22}) + \frac{1}{2}\sqrt{(H_{11}-H_{22})^2 + 4\,|H_{12}|^2} \tag{16-a}$$

$$E_- = \frac{1}{2}(H_{11}+H_{22}) - \frac{1}{2}\sqrt{(H_{11}-H_{22})^2 + 4\,|H_{12}|^2} \tag{16-b}$$

COMMENTS:

(*i*) As we have already said, the eigenvalues (16) can easily be obtained from the characteristic equation of the matrix (H). If we need only the eigenvalues of (H), it is therefore not necessary to introduce the angles θ and φ as we have done here. On the other hand, we shall see in the following section that this method is very useful when we need to use the normalized eigenvectors of H.

(*ii*) It can be verified immediately from formulas (16) that:

$$E_+ + E_- = H_{11} + H_{22} = \text{Tr}\,(H) \tag{17}$$

$$E_+E_- = H_{11}H_{22} - |H_{12}|^2 = \text{Det}\,(H) \tag{18}$$

(*iii*) To have $E_+ = E_-$, we must have $(H_{11} - H_{22})^2 + 4|H_{12}|^2 = 0$; that is, $H_{11} = H_{22}$ and $H_{12} = H_{21} = 0$. A 2×2 Hermitian matrix with a degenerate spectrum is therefore necessarily proportional to the unit matrix.

d. NORMALIZED EIGENVECTORS OF H

Let a and b be the components of $|\psi_+\rangle$ on $|\varphi_1\rangle$ and $|\varphi_2\rangle$. According to (7), (12) and (14-a), they must satisfy:

$$\begin{pmatrix} 1 & \tan\theta\, e^{-i\varphi} \\ \tan\theta\, e^{i\varphi} & -1 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{\cos\theta}\begin{pmatrix} a \\ b \end{pmatrix} \tag{19}$$

which yields:

$$\left(1 - \frac{1}{\cos\theta}\right)a + \tan\theta\, e^{-i\varphi}\, b = 0 \tag{20}$$

that is:

$$-\left(\sin\frac{\theta}{2}\, e^{i\varphi/2}\right)a + \left(\cos\frac{\theta}{2}\, e^{-i\varphi/2}\right)b = 0 \tag{21}$$

The normalized eigenvector $|\psi_+\rangle$ can therefore be written:

$$|\psi_+\rangle = \cos\frac{\theta}{2}\, e^{-i\varphi/2}\,|\varphi_1\rangle + \sin\frac{\theta}{2}\, e^{i\varphi/2}\,|\varphi_2\rangle \tag{22}$$

An analogous calculation would yield:

$$|\psi_-\rangle = -\sin\frac{\theta}{2}\, e^{-i\varphi/2}\,|\varphi_1\rangle + \cos\frac{\theta}{2}\, e^{i\varphi/2}\,|\varphi_2\rangle \tag{23}$$

It can be verified that $|\psi_+\rangle$ and $|\psi_-\rangle$ are orthogonal.

COMMENT:

While the trigonometric functions of the angle θ can be expressed rather simply in terms of the matrix elements H_{ij} [see, for example, formulas (9) and (15)], the same is not true of those of the angle $\theta/2$. Consequently, formulas (22) and (23) for the normalized eigenvectors $|\psi_+\rangle$ and $|\psi_-\rangle$ become complicated when $\cos\theta/2$ and $\sin\theta/2$ are replaced by their expressions in terms of H_{ij}; they are no longer very convenient. It is better to use expressions (22) and (23) directly, keeping the functions $\cos\theta/2$ and $\sin\theta/2$ during the entire calculation involving the normalized eigenvectors of H. Furthermore, the final result of the calculation often involves only functions of the angle θ (see, for example, the calculation of §C-3-b of chapter IV) and, consequently, can be expressed simply in terms of the H_{ij}. Expressions (22) and (23) thus enable us to carry out the intermediate calculations elegantly, avoiding unnecessarily complicated expressions. This is the advantage of the method presented in this complement. Another advantage concerns the physical interpretation and will be discussed in the next complement.

Complement C_{IV}

FICTITIOUS SPIN 1/2 ASSOCIATED WITH A TWO-LEVEL SYSTEM

1. Introduction

Consider a two-level system whose Hamiltonian H is represented, in an orthonormal basis $\{ | \varphi_1 \rangle, | \varphi_2 \rangle \}$, by the Hermitian matrix (H) [formula (1) of complement B_{IV}]★. If we choose $(H_{11} + H_{22})/2$ as the new energy origin, the matrix (H) becomes:

$$(H) = \begin{pmatrix} \frac{1}{2}(H_{11} - H_{22}) & H_{12} \\ H_{21} & -\frac{1}{2}(H_{11} - H_{22}) \end{pmatrix} \tag{1}$$

Although the two-level system under consideration is not necessarily a spin 1/2, we can always associate with it a spin 1/2 whose Hamiltonian H is represented by the same matrix (H) in the $\{ | + \rangle, | - \rangle \}$ basis of eigenstates of the S_z component of this spin. We shall see that (H) can then be interpreted as describing the interaction of this "fictitious spin" with a static magnetic field $\mathbf{B}$, whose direction and modulus are very simply related to the parameters introduced in the preceding complement in the discussion of the diagonalization of (H). Thus it is possible to give a simple physical meaning to these parameters.

Moreover, if the Hamiltonian H is the sum $H = H_0 + W$ of two operators, we shall see that we can associate with H, H_0 and W three magnetic fields, $\mathbf{B}$, $\mathbf{B}_0$ and $\mathbf{b}$, such that $\mathbf{B} = \mathbf{B}_0 + \mathbf{b}$. Introducing the coupling W is equivalent, in terms of fictitious spin, to adding the field $\mathbf{b}$ to $\mathbf{B}_0$. We shall show that this point of view enables us to interpret very simply the different effects studied in § C of chapter IV.

2. Interpretation of the Hamiltonian in terms of fictitious spin

We saw in chapter IV that the Hamiltonian H of the coupling between a spin 1/2 and a magnetic field $\mathbf{B}$, of components B_x, B_y, B_z, can be written:

$$\tilde{H} = -\gamma \, \mathbf{B}.\mathbf{S} = -\gamma(B_x S_x + B_y S_y + B_z S_z) \tag{2}$$

★ We are using the same notation as in complement B_{IV} and chapter IV.

To calculate the matrix associated with this operator, we substitute into this relation the matrices associated with S_x, S_y, S_z [chap. IV, relations (A-15), (A-16), (A-17)]. This immediately yields :

$$(\tilde{H}) = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \tag{3}$$

Therefore, to make matrix (1) identical to $(\tilde{H})$, we must simply choose a "fictitious field" **B** defined by :

$$\begin{cases} B_x = -\dfrac{2}{\gamma\hbar}\,\mathrm{Re}\,H_{12} \\ B_y = \dfrac{2}{\gamma\hbar}\,\mathrm{Im}\,H_{12} \\ B_z = \dfrac{1}{\gamma\hbar}(H_{22} - H_{11}) \end{cases} \tag{4}$$

Note that the modulus $B_\perp$ of the projection $\mathbf{B}_\perp$ of **B** onto the xOy plane is then equal to :

$$B_\perp = \frac{2}{\hbar}\left|\frac{H_{12}}{\gamma}\right| \tag{5}$$

According to formulas (9) and (10) of complement B_{IV}, the angles θ and φ associated with the matrix $(H) = (\tilde{H})$ written in (3) are given by :

$$\begin{cases} \tan\theta = \dfrac{|\gamma B_\perp|}{-\gamma B_z} & 0 \leqslant \theta < \pi \\ -\gamma(B_x + iB_y) = |\gamma B_\perp|\, e^{i\varphi} & 0 \leqslant \varphi < 2\pi \end{cases} \tag{6}$$

The gyromagnetic ratio γ is a simple calculation tool and can have an arbitrary value. If we agree to choose γ negative, relations (6) show that the angles θ and φ associated with the matrix (H) are simply the polar angles of the direction of the field **B** (if we had chosen γ positive, they would be those of the opposite direction).

Finally, we see that we can forget the two-level system with which we started and consider the matrix (H) as representing, in the basis of the eigenstates $|+\rangle$ and $|-\rangle$ of S_z, the Hamiltonian $\tilde{H}$ of a spin 1/2 placed in a field **B** whose components are given by (4). $\tilde{H}$ can also be written :

$$\tilde{H} = \omega S_u \tag{7-a}$$

where S_u is the operator $\mathbf{S}\cdot\mathbf{u}$ which describes the spin component along the direction **u**, whose polar angles are θ and φ, and ω is the Larmor angular velocity :

$$\omega = |\gamma|\,|\mathbf{B}| \tag{7-b}$$

The following table summarizes the various correspondences between the two-level system and the associated fictitious spin 1/2.

Two-level system		Fictitious spin 1/2
$\lvert \varphi_1 \rangle$	$\longleftrightarrow$	$\lvert + \rangle$
$\lvert \varphi_2 \rangle$	$\longleftrightarrow$	$\lvert - \rangle$
$\lvert \psi_+ \rangle$	$\longleftrightarrow$	$\lvert + \rangle_u$
$\lvert \psi_- \rangle$	$\longleftrightarrow$	$\lvert - \rangle_u$
$E_+ - E_-$	$\longleftrightarrow$	$\hbar\omega$
Angles θ and φ introduced in B_{IV}	$\longleftrightarrow$	Polar angles of the fictitious field $\mathbf{B}$
$H_{11} - H_{22}$	$\longleftrightarrow$	$-\gamma\hbar B_z$
$\lvert H_{21} \rvert$	$\longleftrightarrow$	$-\gamma\hbar B_\perp/2$

3. Geometrical interpretation of the various effects discussed in § C of chapter IV

a. FICTITIOUS MAGNETIC FIELDS ASSOCIATED WITH H_0, W AND H

Assume, as in § C of chapter IV, that H appears as the sum of two terms:

$$H = H_0 + W \tag{8}$$

In the $\{ \lvert \varphi_1 \rangle, \lvert \varphi_2 \rangle \}$ basis, the unperturbed Hamiltonian H_0 is represented by a diagonal matrix which, with a suitable choice of the energy origin, is written:

$$(H_0) = \begin{pmatrix} \dfrac{E_1 - E_2}{2} & 0 \\ 0 & -\dfrac{E_1 - E_2}{2} \end{pmatrix} \tag{9}$$

As far as the coupling W is concerned, we assume, as in § C of chapter IV, that it is purely non-diagonal:

$$(W) = \begin{pmatrix} 0 & W_{12} \\ W_{21} & 0 \end{pmatrix} \tag{10}$$

The discussion of the preceding section then enables us to associate with (H_0) and (W) two fields $\mathbf{B}_0$ and $\mathbf{b}$ such that [*cf.* formulas (4) and (5)]:

$$\begin{cases} B_{0z} = \dfrac{E_2 - E_1}{\gamma\hbar} \\ B_{0\perp} = 0 \end{cases} \tag{11}$$

$$\begin{cases} b_z = 0 \\ b_\perp = \dfrac{2}{\hbar}\left| \dfrac{W_{12}}{\gamma} \right| \end{cases} \tag{12}$$

$\mathbf{B}_0$ is therefore parallel to Oz and proportional to $(E_1 - E_2)/2$; $\mathbf{b}$ is perpendicular to Oz and proportional to $|W_{12}|$. Since $(H) = (H_0) + (W)$, the field $\mathbf{B}$ associated with the total Hamiltonian is the vector sum of $\mathbf{B}_0$ and $\mathbf{b}$:

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{b} \tag{13}$$

The three fields $\mathbf{B}_0$, $\mathbf{b}$ and $\mathbf{B}$ are shown in figure 1 ; the angle θ introduced in § C-2-a of chapter IV is the angle between $\mathbf{B}_0$ and $\mathbf{B}$, since $\mathbf{B}_0$ is parallel to Oz.

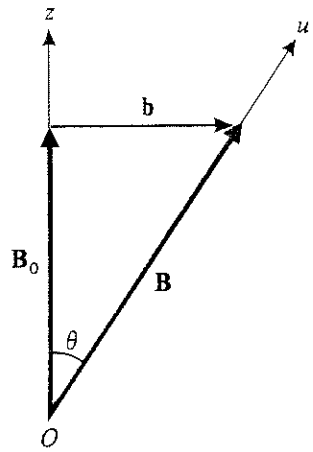

FIGURE 1

Relative disposition of the fictitious fields. $\mathbf{B}_0$ is associated with H_0, $\mathbf{b}$ with W, and $\mathbf{B} = \mathbf{B}_0 + \mathbf{b}$ with the total Hamiltonian $H = H_0 + W$.

The strong coupling condition introduced in § C-2 of chapter IV ($|W_{12}| \gg |E_1 - E_2|$) is equivalent to $|\mathbf{b}| \gg |\mathbf{B}_0|$ (fig. 2-a). The weak coupling condition ($|W_{12}| \ll |E_1 - E_2|$) is equivalent to $|\mathbf{b}| \ll |\mathbf{B}_0|$ (fig. 2-b).

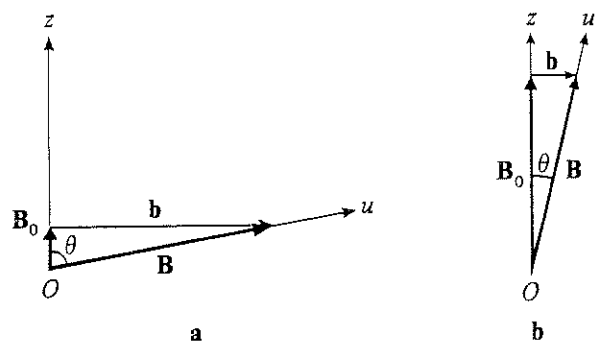

FIGURE 2

Relative disposition of the fictitious fields $\mathbf{B}_0$, $\mathbf{b}$ and $\mathbf{B}$ in the case of strong coupling (fig. a) and weak coupling (fig. b).

b. EFFECT OF COUPLING ON THE EIGENVALUES AND EIGENVECTORS OF THE HAMILTONIAN

$E_1 - E_2$ and $E_+ - E_-$ correspond respectively to the Larmor angular velocities $\omega_0 = |\gamma|\,|\mathbf{B}_0|$ and $\omega = |\gamma|\,|\mathbf{B}|$ in the fields $\mathbf{B}_0$ and $\mathbf{B}$. We see in figure 1 that $\mathbf{B}_0$, $\mathbf{b}$ and $\mathbf{B}$ form a right triangle whose hypotenuse is $\mathbf{B}$; we therefore always have $|\mathbf{B}| \geqslant |\mathbf{B}_0|$, which again shows that $E_+ - E_-$ is always greater than $|E_1 - E_2|$.

For a weak coupling (fig. 2-b), the difference between $|\mathbf{B}|$ and $|\mathbf{B}_0|$ is very small in relative value, being of second order in $|\mathbf{b}|/|\mathbf{B}_0|$. From this we deduce immediately that $E_+ - E_-$ and $E_1 - E_2$ differ in relative value by terms of second order in $|W_{12}|/(E_1 - E_2)$. On the other hand, for a strong coupling (fig. 2-a), $|\mathbf{B}|$ is much larger than $|\mathbf{B}_0|$ and practically equal to $|\mathbf{b}|$; $E_+ - E_-$ is then much larger than $|E_1 - E_2|$ and practically proportional to $|W_{12}|$. We thus find again all the results of § C-2 of chapter IV.

As far as the effect of the coupling on the eigenvectors is concerned, it can also be understood very simply from figures 1 and 2. The eigenvectors of H and H_0 are associated respectively with the eigenvectors of the components of $\mathbf{S}$ on the Ou and Oz axes. These two axes are practically parallel in the case of weak coupling (fig. 2-b) and perpendicular in the case of strong coupling (fig. 2-a). The eigenvectors of S_u and S_z, and, consequently, those of H and H_0, are very close in the first case and very different in the second one.

c. GEOMETRICAL INTERPRETATION OF $\mathscr{P}_{12}(t)$

In terms of fictitious spin, the problem considered in § C-3 of chapter IV can be put in the following way: at time $t = 0$, the fictitious spin associated with the two-level system is in the eigenstate $|+\rangle$ of S_z; $\mathbf{b}$ is added to $\mathbf{B}_0$; what

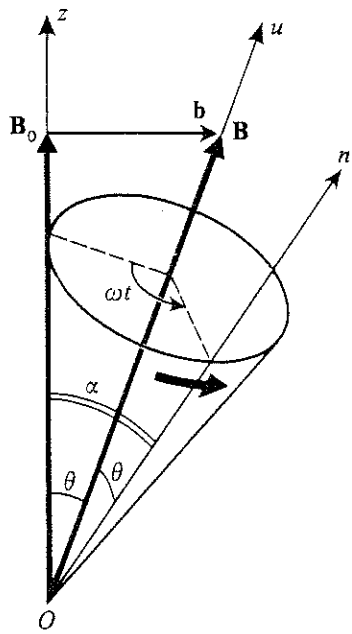

FIGURE 3

Geometrical interpretation of Rabi's formula in terms of fictitious spin. Under the effect of the coupling (represented by b), the spin, initially oriented along Oz, precesses about B; consequently, the probability of finding $-\hbar/2$ in a measurement of its S_z component on Oz is an oscillating function of time.

is the probability $\mathcal{P}_{+\,-}(t)$ of finding the spin in the state $|-\rangle$ at time t? With the correspondences summarized in the table, $\mathcal{P}_{12}(t)$ must be identical to $\mathcal{P}_{+\,-}(t)$.

The calculation of $\mathcal{P}_{+\,-}(t)$ is then very simple since the time evolution of the spin reduces to a Larmor precession about **B** (fig. 3). During this precession, the angle θ between the spin and the direction Ou of **B** remains constant. At time t, the spin points in the direction On, making an angle α with Oz; the angle formed by the (Oz, Ou) and (Ou, On) planes is equal to ωt. A classical formula of spherical trigonometry enables us to write:

$$\cos\alpha = \cos^2\theta + \sin^2\theta\cos\omega t \tag{14}$$

Now, when the spin points in a direction which makes an angle of α with Oz, the probability of finding it in the state $|-\rangle$ of S_z is equal (*cf.* § B-2-b of chapter IV) to $\sin^2\alpha/2 = (1-\cos\alpha)/2$. From this we deduce, using (14), that:

$$\mathcal{P}_{+\,-}(t) = \sin^2\frac{\alpha}{2} = \frac{1}{2}\sin^2\theta(1-\cos\omega t) \tag{15}$$

This result is identical, when we replace ω by $(E_+ - E_-)/\hbar$, to formula (C-31) of chapter IV (Rabi's formula). We have thus given this formula a purely geometrical interpretation.

References and suggestions for further reading:

Abragam (14.1), chap. II, §F; Sargent et al. (15.5), §7-5; Allen (15.7), chap. 2; see also the article by Feynman et al. (1.33).

Complement D_{IV}

SYSTEM OF TWO SPIN 1/2 PARTICLES

In this complement, we intend to use the formalism introduced in §A-2 of chapter IV to describe a system of two spin 1/2 particles. This case is hardly more complicated than that of a single spin 1/2 particle. Its interest, as far as the postulates are concerned, lies in the fact that none of the various spin observables alone constitutes a C.S.C.O. (while this is the case for one spin alone). Thus, we shall be able to consider measurements bearing either on one observable with a degenerate spectrum or simultaneously on two observables. In addition, this study provides a very simple illustration of the concept of a tensor product, introduced in §F of chapter II. We shall be concerned, as in chapter IV, only with the internal degrees of freedom (spin states), and we shall moreover assume that the two particles which constitute the system are not identical (systems of identical particles will be studied in a general way in chapter XIV).

1. Quantum mechanical description

We saw in chapter IV how to describe quantum mechanically the spin state of a spin 1/2 particle. Thus, all we need to do is apply the results of §F of chapter II in order to know how to describe systems of two spin 1/2 particles.

a. STATE SPACE

We shall use the indices 1 and 2 to distinguish between the two particles. When particle (1) is alone, its spin state is defined by a ket which belongs to a two-dimensional state space $\mathcal{E}_S(1)$. Similarly, the spin states of particle (2) alone form a two-dimensional space $\mathcal{E}_S(2)$. We shall designate by $\mathbf{S}_1$ and $\mathbf{S}_2$ the spin observables of particles (1) and (2) respectively. In $\mathcal{E}_S(1)$ [or $\mathcal{E}_S(2)$], we choose as a basis the eigenkets of S_{1z} (or S_{2z}), which we shall denote by $|1:+\rangle$ and $|1:-\rangle$ (or $|2:+\rangle$ and $|2:-\rangle$). The most general ket of $\mathcal{E}_S(1)$ can be written:

$$|\varphi(1)\rangle = \alpha_1 |1:+\rangle + \beta_1 |1:-\rangle \tag{1}$$

and that of $\mathscr{E}_S(2)$:

$$|\chi(2)\rangle = \alpha_2 |2:+\rangle + \beta_2 |2:-\rangle \tag{2}$$

(α_1, β_1, α_2, β_2 are arbitrary complex numbers).

When we join the two particles to make a single system, the state space $\mathscr{E}_S$ of such a system is the tensor product of the two preceding spaces:

$$\mathscr{E}_S = \mathscr{E}_S(1) \otimes \mathscr{E}_S(2) \tag{3}$$

In the first place, this means that a basis of $\mathscr{E}_S$ can be obtained by multiplying tensorially the two bases defined above for $\mathscr{E}_S(1)$ and $\mathscr{E}_S(2)$. We shall use the following notation :

$$\begin{aligned} |++\rangle &= |1:+\rangle |2:+\rangle \\ |+-\rangle &= |1:+\rangle |2:-\rangle \\ |-+\rangle &= |1:-\rangle |2:+\rangle \\ |--\rangle &= |1:-\rangle |2:-\rangle \end{aligned} \tag{4}$$

In the state $|+-\rangle$, for example, the component along Oz of the spin of particle (1) is $+\hbar/2$, with absolute certainty; that of the spin of particle (2) is $-\hbar/2$, with absolute certainty. We shall agree here to denote by $\langle +- |$ the conjugate bra of the ket $|+-\rangle$; the order of the symbols is therefore the same in the ket and in the bra: the first symbol is always associated with particle (1) and the second, with particle (2).

The space $\mathscr{E}_S$ is therefore four-dimensional. Since the $\{|1:\pm\rangle\}$ and $\{|2:\pm\rangle\}$ bases are orthonormal in $\mathscr{E}_S(1)$ and $\mathscr{E}_S(2)$ respectively, the basis (4) is orthonormal in $\mathscr{E}_S$:

$$\langle \varepsilon_1\varepsilon_2 | \varepsilon_1'\varepsilon_2' \rangle = \delta_{\varepsilon_1\varepsilon_1'}\delta_{\varepsilon_2\varepsilon_2'} \tag{5}$$

(ε_1, ε_2, ε_1', ε_2' are to be replaced by $+$ or $-$ depending on the case; $\delta_{\varepsilon\varepsilon'}$ is equal to 1 if ε and ε' are identical and 0 if they are different). The system of vectors (4) also satisfies a closure relation in $\mathscr{E}_S$:

$$\sum_{\varepsilon_1\varepsilon_2} |\varepsilon_1\varepsilon_2\rangle\langle\varepsilon_1\varepsilon_2| = |++\rangle\langle++| + |+-\rangle\langle+-| + |-+\rangle\langle-+| + |--\rangle\langle--| = \mathbb{1} \tag{6}$$

b. COMPLETE SETS OF COMMUTING OBSERVABLES

We extend into $\mathscr{E}_S$ the observables $\mathbf{S}_1$ and $\mathbf{S}_2$ which were originally defined in $\mathscr{E}_S(1)$ and $\mathscr{E}_S(2)$ (as in chapter II, we shall continue to denote these extensions by $\mathbf{S}_1$ and $\mathbf{S}_2$). Their action on the kets of the basis (4) is simple: the components of $\mathbf{S}_1$, for example, act only on the part of the ket related to particle (1). In particular, the vectors of the basis (4) are simultaneous eigenvectors of S_{1z} and S_{2z}:

$$\begin{aligned} S_{1z} |\varepsilon_1\varepsilon_2\rangle &= \frac{\hbar}{2}\varepsilon_1 |\varepsilon_1\varepsilon_2\rangle \\ S_{2z} |\varepsilon_1\varepsilon_2\rangle &= \frac{\hbar}{2}\varepsilon_2 |\varepsilon_1\varepsilon_2\rangle \end{aligned} \tag{7}$$

For the other components of $\mathbf{S}_1$ and $\mathbf{S}_2$, we apply the formulas given in §A-2 of chapter IV. For example, we know from relation (A-16) of chapter IV how S_{1x} acts on the kets $|1:\pm\rangle$:

$$\begin{aligned} S_{1x}|1:+\rangle &= \frac{\hbar}{2}|1:-\rangle \\ S_{1x}|1:-\rangle &= \frac{\hbar}{2}|1:+\rangle \end{aligned} \tag{8}$$

From this we deduce the action of S_{1x} on the kets (4):

$$\begin{aligned} S_{1x}|++\rangle &= \frac{\hbar}{2}|-+\rangle \\ S_{1x}|+-\rangle &= \frac{\hbar}{2}|--\rangle \\ S_{1x}|-+\rangle &= \frac{\hbar}{2}|++\rangle \\ S_{1x}|--\rangle &= \frac{\hbar}{2}|+-\rangle \end{aligned} \tag{9}$$

It is then easy to verify that, although the three components of $\mathbf{S}_1$ (or of $\mathbf{S}_2$) do not commute with each other, *any component of* $\mathbf{S}_1$ *commutes with any component of* $\mathbf{S}_2$.

In $\mathcal{E}_S(1)$, the observable S_{1z} alone constituted a C.S.C.O., and the same was true of S_{2z} in $\mathcal{E}_S(2)$. In $\mathcal{E}_S$, the eigenvalues of S_{1z} and S_{2z} remain $\pm\hbar/2$, but each of them is two-fold degenerate. To the eigenvalue $+\hbar/2$ of S_{1z}, for example, correspond two orthogonal vectors, $|++\rangle$ and $|+-\rangle$ [formulas (7)] and all their linear combinations. Therefore, in $\mathcal{E}_S$, neither S_{1z} nor S_{2z} (taken separately) constitutes a C.S.C.O. On the other hand, the set $\{S_{1z}, S_{2z}\}$ is a C.S.C.O. in $\mathcal{E}_S$, as can be seen from formulas (7).

This is obviously not the only C.S.C.O. that can be constructed. For example, another one is $\{S_{1z}, S_{2x}\}$. These two observables commute, as we noted above, and each of them constitutes a C.S.C.O. in the space in which it was initially defined. The eigenvectors which are common to S_{1z} and S_{2x} are obtained by taking the tensor product of their respective eigenvectors in $\mathcal{E}_S(1)$ and $\mathcal{E}_S(2)$. Using relation (A-20) of chapter IV, we find:

$$\begin{aligned} |1:+\rangle|2:+\rangle_x &= \frac{1}{\sqrt{2}}[|++\rangle+|+-\rangle] \\ |1:+\rangle|2:-\rangle_x &= \frac{1}{\sqrt{2}}[|++\rangle-|+-\rangle] \\ |1:-\rangle|2:+\rangle_x &= \frac{1}{\sqrt{2}}[|-+\rangle+|--\rangle] \\ |1:-\rangle|2:-\rangle_x &= \frac{1}{\sqrt{2}}[|-+\rangle-|--\rangle] \end{aligned} \tag{10}$$

c. THE MOST GENERAL STATE

The vectors (4) were obtained by multiplying tensorially a ket of $\mathcal{E}_S(1)$ and a ket of $\mathcal{E}_S(2)$. More generally, using an arbitrary ket of $\mathcal{E}_S(1)$ [such as (1)] and an arbitrary ket of $\mathcal{E}_S(2)$ [such as (2)], we can construct a ket of $\mathcal{E}_S$:

$$|\varphi(1)\rangle |\chi(2)\rangle = \alpha_1\alpha_2 |++\rangle + \alpha_1\beta_2 |+-\rangle + \alpha_2\beta_1 |-+\rangle + \beta_1\beta_2 |--\rangle \quad (11)$$

The components of such a ket in the basis (4) are the products of the components of $|\varphi(1)\rangle$ and $|\chi(2)\rangle$ in the bases of $\mathcal{E}_S(1)$ and $\mathcal{E}_S(2)$ which were used to construct (4).

But *all the kets of $\mathcal{E}_S$ are not tensor products.* The most general ket of $\mathcal{E}_S$ is an arbitrary linear combination of the basis vectors:

$$|\psi\rangle = \alpha |++\rangle + \beta |+-\rangle + \gamma |-+\rangle + \delta |--\rangle \quad (12)$$

If we want to normalize $|\psi\rangle$, we must choose:

$$|\alpha|^2 + |\beta|^2 + |\gamma|^2 + |\delta|^2 = 1 \quad (13)$$

Given $|\psi\rangle$, it is not in general possible to find two kets $|\varphi(1)\rangle$ and $|\chi(2)\rangle$ of which it is the tensor product. For (12) to be of the form (11), we must have, in particular:

$$\frac{\alpha}{\beta} = \frac{\gamma}{\delta} \quad (14)$$

and this condition is not necessarily fulfilled.

2. Prediction of the measurement results

We are now going to envisage a certain number of measurements which can be performed on a system of two spin 1/2 particles and we shall calculate the predictions furnished by the postulates for each of them. We shall assume each time that the state of the system immediately before the measurement is described by the normalized ket (12).

a. MEASUREMENTS BEARING SIMULTANEOUSLY ON THE TWO SPINS

Since any component of $\mathbf{S}_1$ commutes with any component of $\mathbf{S}_2$, we can envisage measuring them simultaneously (chap. III, § C-6-a). To calculate the predictions related to such measurements, all we need to do is use the eigenvectors common to the two observables.

α. *First example*

First of all, let us assume that we are simultaneously measuring S_{1z} and S_{2z}. What are the probabilities of the various results that can be obtained?

Since the set $\{ S_{1z}, S_{2z} \}$ is a C.S.C.O., there exists only one state associated with each measurement result. If the system is in the state (12) before the measurement, we can therefore find:

$$\begin{aligned}
&+\frac{\hbar}{2} \text{ for } S_{1z} \text{ and } +\frac{\hbar}{2} \text{ for } S_{2z}, \text{ with the probability } |\langle + + | \psi \rangle|^2 = |\alpha|^2 \\
&+\frac{\hbar}{2} \quad " \quad -\frac{\hbar}{2} \quad " \quad " \quad |\langle + - | \psi \rangle|^2 = |\beta|^2 \\
&-\frac{\hbar}{2} \quad " \quad +\frac{\hbar}{2} \quad " \quad " \quad |\langle - + | \psi \rangle|^2 = |\gamma|^2 \\
&-\frac{\hbar}{2} \quad " \quad -\frac{\hbar}{2} \quad " \quad " \quad |\langle - - | \psi \rangle|^2 = |\delta|^2 \qquad (15)
\end{aligned}$$

β. *Second example*

We now measure S_{1y} and S_{2z}. What is the probability of obtaining $+\hbar/2$ for each of the two observables?

Here again, $\{ S_{1y}, S_{2z} \}$ constitutes a C.S.C.O. The eigenvector common to S_{1y} and S_{2z} which corresponds to the eigenvalues $+\hbar/2$ and $+\hbar/2$ is the tensor product of the vector $|1: + \rangle_y$ and the vector $|2: + \rangle$:

$$|1: + \rangle_y |2: + \rangle = \frac{1}{\sqrt{2}} [\, |+ + \rangle + i |- + \rangle] \qquad (16)$$

Applying the fourth postulate of chapter III, we find that the probability we are looking for is:

$$\begin{aligned}
\mathcal{P} &= \left| \frac{1}{\sqrt{2}} \left[\langle + + | - i \langle - + | \right] | \psi \rangle \right|^2 \\
&= \frac{1}{2} |\alpha - i\gamma|^2 \qquad (17)
\end{aligned}$$

The result therefore appears in the form of a "square of a sum"★.

After the measurement, if we have actually found $+\hbar/2$ for S_{1y} and $+\hbar/2$ for S_{2z}, the system is in the state (16).

b. MEASUREMENTS BEARING ON ONE SPIN ALONE

It is obviously possible to measure only one component of one of the two spins. In this case, since none of these components constitutes by itself a C.S.C.O., there exist several eigenvectors corresponding to the same measurement result, and the corresponding probability will be a "sum of squares".

★ It must be remembered that the sign of i changes when we go from (16) to the conjugate bra. If this were to be forgotten, the result obtained would be incorrect ($|\alpha + i\gamma|^2 \neq |\alpha - i\gamma|^2$ since α/γ is not in general real).

α. *First example*

We measure only S_{1z}. What results can be found, and with what probabilities?

The possible results are the eigenvalues $\pm \hbar/2$ of S_{1z}. Each of them is doubly degenerate. In the associated eigensubspace, we choose an orthonormal basis: we can, for example, take $\{ |++\rangle, |+-\rangle \}$ for $+\hbar/2$ and $\{ |-+\rangle, |--\rangle \}$ for $-\hbar/2$. We then obtain:

$$\begin{aligned} \mathscr{P}\left(+\frac{\hbar}{2}\right) &= |\langle ++|\psi\rangle|^2 + |\langle +-|\psi\rangle|^2 \\ &= |\alpha|^2 + |\beta|^2 \\ \mathscr{P}\left(-\frac{\hbar}{2}\right) &= |\langle -+|\psi\rangle|^2 + |\langle --|\psi\rangle|^2 \\ &= |\gamma|^2 + |\delta|^2 \end{aligned} \tag{18}$$

COMMENT:

Since we are not performing any measurement on the spin (2), the choice of the basis in $\mathscr{E}_S(2)$ is arbitrary. We can, for example, choose as a basis of the eigensubspace of S_{1z} associated with the eigenvalue $+\hbar/2$ the vectors:

$$|1:+\rangle |2:\pm\rangle_x = \frac{1}{\sqrt{2}}[|++\rangle \pm |+-\rangle] \tag{19}$$

which again gives us:

$$\begin{aligned} \mathscr{P}\left(+\frac{\hbar}{2}\right) &= \frac{1}{2}|\alpha+\beta|^2 + \frac{1}{2}|\alpha-\beta|^2 \\ &= |\alpha|^2 + |\beta|^2 \end{aligned} \tag{20}$$

The general proof of the fact that the probability obtained is independent (in the case of a degenerate eigenvalue) of the choice of the basis in the corresponding eigensubspace was given in § B-3-b-α of chapter III.

β. *Second example*

Now it is S_{2x} that we want to measure. What is the probability of obtaining $-\hbar/2$?

The eigensubspace associated with the eigenvalue $-\hbar/2$ of S_{2x} is two-dimensional. We can choose for a basis in it:

$$\begin{aligned} |1:+\rangle |2:-\rangle_x &= \frac{1}{\sqrt{2}}[|++\rangle - |+-\rangle] \\ |1:-\rangle |2:-\rangle_x &= \frac{1}{\sqrt{2}}[|-+\rangle - |--\rangle] \end{aligned} \tag{21}$$

We then find:

$$\begin{aligned} \mathscr{P} &= \left|\frac{1}{\sqrt{2}}[\langle ++| - \langle +-|]|\psi\rangle\right|^2 + \left|\frac{1}{\sqrt{2}}[\langle -+| - \langle --|]|\psi\rangle\right|^2 \\ &= \frac{1}{2}|\alpha-\beta|^2 + \frac{1}{2}|\gamma-\delta|^2 \end{aligned} \tag{22}$$

In this result, each of the terms of the "sum of squares" is itself the "square of a sum".

If the measurement actually yields $-\hbar/2$, the state $|\psi'\rangle$ of the system immediately after this measurement is the (normalized) projection of $|\psi\rangle$ onto the corresponding eigensubspace. We have just calculated the components of $|\psi\rangle$ on the basis vectors (21) of this subspace : they are equal, respectively, to $\frac{1}{\sqrt{2}}(\alpha - \beta)$ and $\frac{1}{\sqrt{2}}(\gamma - \delta)$. Consequently :

$$|\psi'\rangle = \frac{1}{\sqrt{\frac{1}{2}|\alpha - \beta|^2 + \frac{1}{2}|\gamma - \delta|^2}} \left[\frac{1}{2}(\alpha - \beta)(|++\rangle - |+-\rangle) + \frac{1}{2}(\gamma - \delta)(|-+\rangle - |--\rangle)\right] \quad (23)$$

COMMENT :

We have considered, in this complement, only the components of $\mathbf{S}_1$ and $\mathbf{S}_2$ on the coordinate axes. It is obviously possible to measure their components $\mathbf{S}_1 \cdot \mathbf{u}$ and $\mathbf{S}_2 \cdot \mathbf{v}$ on arbitrary unit vectors $\mathbf{u}$ and $\mathbf{v}$. The reasoning is the same as above.

Complement E_{IV}

SPIN 1/2 DENSITY MATRIX

1. Introduction

The aim of this complement is to illustrate the general considerations developed in complement E_{III}, using a very simple physical system, that of a spin 1/2. We are going to study the density matrices which describe a spin 1/2 in a certain number of cases : perfectly polarized spin (pure case), unpolarized or partially polarized spin (statistical mixture). We shall thus be able to verify and interpret the general properties stated in complement E_{III}. In addition, we shall see that the expansion of the density matrix in terms of the Pauli matrices can be expressed very simply as a function of the mean values of the various spin components.

2. Density matrix of a perfectly polarized spin (pure case)

Consider a spin 1/2, coming out of an "atomic polarizer" of the type described in § B of chapter IV, which is in the eigenstate $|+\rangle_u$ (eigenvalue $+\hbar/2$) of the $\mathbf{S}\cdot\mathbf{u}$ component of the spin (recall that the polar angles of the unit vector $\mathbf{u}$ are θ and φ). The spin state is then perfectly well-known and is written [*cf.* formula (A-22-a) of chapter IV] :

$$|\psi\rangle = \cos\frac{\theta}{2}\,e^{-i\varphi/2}\,|+\rangle + \sin\frac{\theta}{2}\,e^{i\varphi/2}|-\rangle \tag{1}$$

We saw in complement E_{III} that, by definition, such a situation corresponds to a pure case. We shall say that the beam which leaves the "polarizer" is perfectly polarized. Recall also that, for each spin, the mean value $\langle\mathbf{S}\rangle$ is equal to $\frac{\hbar}{2}\mathbf{u}$ [chap. IV, relations (B-14)].

It is simple to write, in the $\{|+\rangle, |-\rangle\}$ basis, the density matrix $\rho(\theta, \varphi)$ corresponding to the state (1). We write the matrix of the projector onto this state :

$$\rho(\theta,\varphi) = \begin{pmatrix} \cos^2\frac{\theta}{2} & \sin\frac{\theta}{2}\cos\frac{\theta}{2}\,e^{-i\varphi} \\ \sin\frac{\theta}{2}\cos\frac{\theta}{2}\,e^{i\varphi} & \sin^2\frac{\theta}{2} \end{pmatrix} \tag{2}$$

This matrix is generally non-diagonal. The "populations" ρ_{++} and ρ_{--} have a very simple physical significance. Their difference is equal to $\cos\theta = 2\langle S_z\rangle/\hbar$ [*cf.* equations (B-14) of chapter IV], and their sum is, of course, equal to 1. The populations are therefore related to the longitudinal polarization $\langle S_z\rangle$. Similarly, the modulus of the "coherences" ρ_{+-} and ρ_{-+} is $|\rho_{+-}| = |\rho_{-+}| = \frac{1}{2}\sin\theta = \frac{1}{\hbar}|\langle \mathbf{S}_\perp\rangle|$ (where $\langle \mathbf{S}_\perp\rangle$ is the projection of $\langle \mathbf{S}\rangle$ onto the xOy plane). The argument of ρ_{-+} is φ, that is, the angle between $\langle \mathbf{S}_\perp\rangle$ and Ox : the coherences are therefore related to the transverse polarization $\langle \mathbf{S}_\perp\rangle$.

It can also be verified that :

$$[\rho(\theta, \varphi)]^2 = \rho(\theta, \varphi) \tag{3}$$

a relation characteristic of a pure state.

3. Example of a statistical mixture: unpolarized spin

Now let us consider the spin of a silver atom leaving a furnace, such as the one in figure 1 of chapter IV, and which has not passed through an "atomic polarizer" (the spin has not been prepared in a particular state). The only information we then possess about this spin is the following : it can point in any direction of space, and all directions are equally probable. With the notation of complement E_{III}, such a situation corresponds to a statistical mixture of the states $|+\rangle_u$ with equal weights. Formula (28) of complement E_{III} defines the density matrix ρ which corresponds to this case. Nevertheless, the discrete sum $\sum_k$ must here be replaced by an integral over all the possible directions :

$$\rho = \frac{1}{4\pi}\int d\Omega\, \rho(\theta, \varphi) = \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta\, \rho(\theta, \varphi) \tag{4}$$

(the factor $1/4\pi$ insures the normalization of the probabilities associated with the various directions). The integrals which give the matrix elements of ρ are simple to calculate and lead to the following result :

$$\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \tag{5}$$

It is easy to deduce from (5) that $\rho^2 = \rho/2$, which shows that, in the case of a statistical mixture of states, ρ^2 is different from ρ.

In addition, if we calculate from (5) the mean values of S_x, S_y, S_z, we obtain :

$$\langle S_i\rangle = \mathrm{Tr}\,[\rho S_i] = \frac{1}{2}\mathrm{Tr}\, S_i = 0 \qquad i = x, y, z \tag{6}$$

We again find the fact that the spin is unpolarized : since all the directions are equivalent, the mean value of the spin is zero.

COMMENTS:

(*i*) It is clear from this example how the non-diagonal elements (coherences) of ρ can disappear from the summation over the various states of the statistical mixture. As we saw in § 2, the coherences ρ_{+-} and ρ_{-+} are related to the transverse polarization $\langle \mathbf{S}_\perp \rangle$ of the spin. Upon summing the vectors $\langle \mathbf{S}_\perp \rangle$ corresponding to all (equiprobable) directions of the xOy plane, we obviously find a null result.

(*ii*) The case of unpolarized spin is also very instructive, since it helps us to understand the impossibility of describing a statistical mixture by an "average state vector". Assume that we are trying to choose α and β so that the vector:

$$|\psi\rangle = \alpha|+\rangle + \beta|-\rangle \tag{7}$$

with :

$$|\alpha|^2 + |\beta|^2 = 1 \tag{8}$$

represents an unpolarized spin, for which $\langle S_x \rangle$, $\langle S_y \rangle$ and $\langle S_z \rangle$ are zero. A simple calculation gives:

$$\begin{aligned} \langle S_x \rangle &= \frac{\hbar}{2}(\alpha^*\beta + \alpha\beta^*) \\ \langle S_y \rangle &= \frac{\hbar}{2i}(\alpha^*\beta - \alpha\beta^*) \\ \langle S_z \rangle &= \frac{\hbar}{2}(\alpha^*\alpha - \beta^*\beta) \end{aligned} \tag{9}$$

If we want to make $\langle S_x \rangle$ zero, we must choose α and β so as to make $\alpha^*\beta$ a pure imaginary; similarly, $\alpha^*\beta$ must be real for $\langle S_y \rangle$ to be zero. We must therefore have $\alpha^*\beta = 0$; that is:

$$\begin{aligned} &\text{either } \alpha = 0, \text{ which implies } |\beta| = 1 \text{ and } \langle S_z \rangle = -\hbar/2 \\ &\text{or} \quad \beta = 0, \text{ which implies } |\alpha| = 1 \text{ and } \langle S_z \rangle = \hbar/2 \end{aligned}$$

Therefore, $\langle S_z \rangle$, $\langle S_x \rangle$ and $\langle S_y \rangle$ cannot all be zero at the same time; consequently, the state (7) cannot represent an unpolarized spin.

Furthermore, the discussion of § B-1-c of chapter IV shows that for any α and β which satisfy (8), one can always associate with them two angles θ and φ which fix a direction $\mathbf{u}$ such that $|\psi\rangle$ is an eigenvector of $\mathbf{S} \cdot \mathbf{u}$ with the eigenvalue $+\hbar/2$. Thus we see directly that a state such as (7) always describes a spin which is perfectly polarized in a certain direction of space.

(*iii*) The density matrix (5) represents a statistical mixture of the various states $|+\rangle_u$, all the directions $\mathbf{u}$ being equiprobable (this is how we obtained it). We could, however, imagine other statistical mixtures which would lead to the same density matrix : for example, a statistical mixture of equal proportions of the states $|+\rangle$ and $|-\rangle$, or a statistical mixture of equal proportions of three states $|+\rangle_u$ such that the tips of the three corresponding vectors $\mathbf{u}$ are the vertices of an equilateral triangle centered at O. Thus we see that the same density matrix can be obtained in several different ways. In

fact, since all the physical predictions depend only on the density matrix, it is impossible to distinguish physically between the various types of statistical mixtures which lead to the same density matrix. They must be considered to be different expressions for the same incomplete information which we possess about the system.

4. Spin 1/2 in thermodynamic equilibrium in a static field

Consider a spin 1/2 placed in a static field $\mathbf{B}_0$ parallel to Oz. We saw in § B-3-a of chapter IV that the stationary states of this spin are the states $|+\rangle$ and $|-\rangle$, of energies $+\hbar\omega_0/2$ and $-\hbar\omega_0/2$ (with $\omega_0 = -\gamma B_0$, where γ is the gyromagnetic ratio of the spin). If we know only that the system is in thermodynamic equilibrium at the temperature T, we can assert that it has a probability $Z^{-1}\,e^{-\hbar\omega_0/2kT}$ of being in the state $|+\rangle$ and $Z^{-1}\,e^{+\hbar\omega_0/2kT}$ of being in the state $|-\rangle$, where $Z = e^{-\hbar\omega_0/2kT} + e^{+\hbar\omega_0/2kT}$ is a normalization factor (Z is called the "partition function"). We have here another example of a statistical mixture, described by the density matrix:

$$\rho = Z^{-1}\begin{pmatrix} e^{-\hbar\omega_0/2kT} & 0 \\ 0 & e^{+\hbar\omega_0/2kT} \end{pmatrix} \tag{10}$$

Once more, it is easy to verify that $\rho^2 \neq \rho$. The non-diagonal elements are zero since all directions perpendicular to $\mathbf{B}_0$ (that is, to Oz) and fixed by the angle φ are equivalent.

From (10), it is easy to calculate:

$$\begin{aligned} \langle S_x \rangle &= \mathrm{Tr}\,(\rho S_x) = 0 \\ \langle S_y \rangle &= \mathrm{Tr}\,(\rho S_y) = 0 \\ \langle S_z \rangle &= \mathrm{Tr}\,(\rho S_z) = -\frac{\hbar}{2}\,\tanh\left(\frac{\hbar\omega_0}{2kT}\right) \end{aligned} \tag{11}$$

We see that the spin acquires a polarization parallel to the field in which it is placed. The larger ω_0 (that is, B_0) and the lower the temperature T, the greater the polarization. Since $|\tanh x| < 1$, this polarization is less than the value $\hbar/2$ which corresponds to a spin which is perfectly polarized along Oz. (10) can therefore be said to describe a spin which is "partially polarized" along Oz.

COMMENT:

The magnetization $\langle M_z \rangle$ is equal to $\gamma \langle S_z \rangle$. It is possible to calculate from (11) the paramagnetic susceptibility χ of the spin, defined by:

$$\langle M_z \rangle = \gamma \langle S_z \rangle = \chi B_0 \tag{12}$$

We find (Brillouin's formula):

$$\chi = \frac{\hbar\gamma}{2B_0}\tanh\left(\frac{\hbar\gamma B_0}{2kT}\right) \tag{13}$$

5. Expansion of the density matrix in terms of the Pauli matrices

We saw in complement A_{IV} that the unit matrix I and the Pauli matrices σ_x, σ_y and σ_z form a convenient basis for expanding a 2×2 matrix. We therefore set, for the density matrix ρ of a spin 1/2 :

$$\rho = a_0 I + \mathbf{a} \cdot \boldsymbol{\sigma} \tag{14}$$

where the coefficients a_i are given by [*cf.* complement A_{IV}, relations (23)]:

$$\begin{aligned} a_0 &= \frac{1}{2} \mathrm{Tr}\, \rho \\ a_x &= \frac{1}{2} \mathrm{Tr}\, (\rho \sigma_x) = \frac{1}{\hbar} \mathrm{Tr}\, (\rho S_x) \\ a_y &= \frac{1}{2} \mathrm{Tr}\, (\rho \sigma_y) = \frac{1}{\hbar} \mathrm{Tr}\, (\rho S_y) \\ a_z &= \frac{1}{2} \mathrm{Tr}\, (\rho \sigma_z) = \frac{1}{\hbar} \mathrm{Tr}\, (\rho S_z) \end{aligned} \tag{15}$$

Thus we have :

$$\begin{aligned} a_0 &= \frac{1}{2} \\ \mathbf{a} &= \frac{1}{\hbar} \langle \mathbf{S} \rangle \end{aligned} \tag{16}$$

and ρ can be written :

$$\rho = \frac{1}{2} I + \frac{1}{\hbar} \langle \mathbf{S} \rangle \cdot \boldsymbol{\sigma} \tag{17}$$

Therefore, the density matrix ρ of a spin 1/2 can be expressed very simply in terms of the mean value $\langle \mathbf{S} \rangle$ of the spin.

COMMENT :

Let us square expression (17). We obtain, using identity (17) of complement A_{IV} :

$$\rho^2 = \frac{1}{4} I + \frac{1}{\hbar^2} \langle \mathbf{S} \rangle^2 I + \frac{1}{\hbar} \langle \mathbf{S} \rangle \cdot \boldsymbol{\sigma} \tag{18}$$

The condition $\rho^2 = \rho$, characteristic of the pure case, is therefore equivalent, for a spin 1/2, to the condition :

$$\langle \mathbf{S} \rangle^2 = \frac{\hbar^2}{4} \tag{19}$$

This condition is obviously not satisfied for an unpolarized spin ($\langle \mathbf{S} \rangle$ is then zero) or for a spin in thermodynamic equilibrium (we saw in §4 that in this case $|\langle \mathbf{S} \rangle| < \hbar/2$). On the other hand, it can be verified, using formulas (B-14) of chapter IV, that, for a spin in the state $|\psi\rangle$ given in (1), $\langle \mathbf{S} \rangle^2$ is indeed equal to $\hbar^2/4$.

References and suggestions for further reading:

Abragam (14.1), chap. II, § C.

Complement F_{IV}

SPIN 1/2 PARTICLE IN A STATIC MAGNETIC FIELD AND A ROTATING FIELD: MAGNETIC RESONANCE

In chapter IV, we used quantum mechanics to study the evolution of a spin 1/2 in a static magnetic field. In this complement, we shall consider the case of a spin 1/2 simultaneously subjected to several magnetic fields, some of which can be time dependent, as is the case in magnetic resonance experiments. Before attacking this problem quantum mechanically, we shall briefly review several results obtained using classical mechanics.

1. Classical treatment; rotating reference frame

a. MOTION IN A STATIC FIELD; LARMOR PRECESSION

Consider a system of angular momentum $\mathbf{j}$ which possesses a magnetic moment $\mathbf{m} = \gamma\mathbf{j}$ collinear with $\mathbf{j}$ (the constant γ is the gyromagnetic ratio of the system), placed in a static magnetic field $\mathbf{B}_0$, which exerts a torque $\boldsymbol{m} \times \mathbf{B}_0$ on the system. The classical equation of motion of $\mathbf{j}$ is:

$$\frac{d\mathbf{j}}{dt} = \mathbf{m} \times \mathbf{B}_0 \tag{1}$$

or:

$$\frac{d}{dt}\mathbf{m}(t) = \gamma\mathbf{m}(t) \times \mathbf{B}_0 \tag{2}$$

Performing a scalar multiplication of both sides of this equation by either $\mathbf{m}(t)$ or $\mathbf{B}_0$, we obtain:

$$\frac{d}{dt}[\mathbf{m}(t)]^2 = 0 \tag{3}$$

$$\frac{d}{dt}[\mathbf{m}(t) \cdot \mathbf{B}_0] = 0 \tag{4}$$

$\mathbf{m}(t)$ therefore evolves with a constant modulus, maintaining a constant angle with $\mathbf{B}_0$. If we project equation (2) onto the plane perpendicular to $\mathbf{B}_0$, we see that $\mathbf{m}(t)$ rotates about $\mathbf{B}_0$ (Larmor precession) with an angular velocity of $\omega_0 = -\gamma B_0$ (the rotation is counterclockwise if γ is positive).

b. INFLUENCE OF A ROTATING FIELD; RESONANCE

Now assume that we add to the static field $\mathbf{B}_0$ a field $\mathbf{B}_1(t)$, perpendicular to $\mathbf{B}_0$, and which is of constant modulus and rotates about $\mathbf{B}_0$ with an angular velocity ω (*cf.* fig. 1). We set:

$$\begin{aligned} \omega_0 &= -\gamma B_0 \\ \omega_1 &= -\gamma B_1 \end{aligned} \tag{5}$$

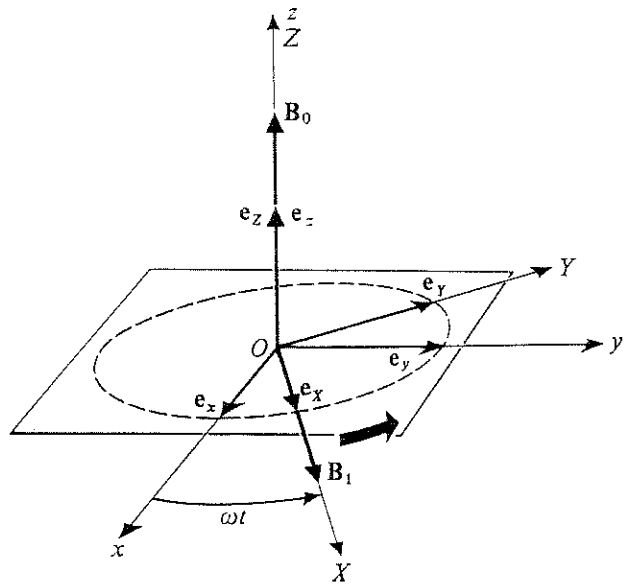

FIGURE 1

$Oxyz$ is a fixed coordinate system. The static magnetic field $\mathbf{B}_0$ is directed along the Oz axis. The $OXYZ$ system [the OX axis is the direction of the field $\mathbf{B}_1(t)$] rotates about Oz with the angular velocity ω.

We shall designate by $Oxyz$ (unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$) a fixed coordinate system, whose Oz axis is the direction of the field $\mathbf{B}_0$, and by $OXYZ$ (unit vectors $\mathbf{e}_X$, $\mathbf{e}_Y$, $\mathbf{e}_Z$), the axes obtained from $Oxyz$ by rotation through an angle ωt about Oz [OX is the direction of the rotating field $\mathbf{B}_1(t)$]. The equation of motion of $\mathbf{m}(t)$ in the presence of the total field $\mathbf{B}(t) = \mathbf{B}_0 + \mathbf{B}_1(t)$ then becomes:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{m}(t) = \gamma\, \mathbf{m}(t) \times [\mathbf{B}_0 + \mathbf{B}_1(t)] \tag{6}$$

To solve this equation, it is convenient to place ourselves, not in the absolute reference frame $Oxyz$, but in the rotating reference frame $OXYZ$, with respect to which the relative velocity of the vector $\mathbf{m}(t)$ is:

$$\left(\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t}\right)_{\mathrm{rel}} = \frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t} - \omega\, \mathbf{e}_Z \times \mathbf{m}(t) \tag{7}$$

Let us set :

$$\Delta\omega = \omega - \omega_0 \tag{8}$$

Substituting (6) into (7), we obtain:

$$\left(\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t}\right)_{\text{rel}} = \mathbf{m}(t) \times [\Delta\omega\, \mathbf{e}_Z - \omega_1 \mathbf{e}_X] \tag{9}$$

This equation is much simpler to solve than equation (6), since the coefficients of the right-hand side are now time-independent. Moreover, its form is analogous to that of (2) : the relative motion of the vector $\mathbf{m}(t)$ is therefore a rotation about the "effective field" $\mathbf{B}_{\text{eff}}$ (which is static with respect to the rotating reference frame), given by (*cf.* fig. 2):

$$\mathbf{B}_{\text{eff}} = \frac{1}{\gamma}[\Delta\omega\, \mathbf{e}_Z - \omega_1 \mathbf{e}_X] \tag{10}$$

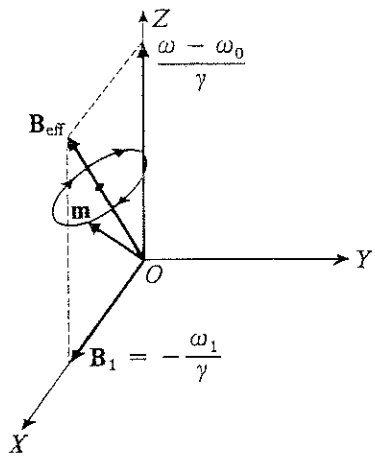

FIGURE 2

In the rotating reference frame $OXYZ$, the effective field $\mathbf{B}_{\text{eff}}$ has a fixed direction, about which the magnetic moment $\mathbf{m}(t)$ rotates with a constant angular velocity (precession in the rotating reference frame).

To obtain the absolute motion of $\mathbf{m}(t)$, we must combine this precession about $\mathbf{B}_{\text{eff}}$ with a rotation about Oz of angular velocity ω.

These first results already enable us to understand the essence of the magnetic resonance phenomenon. Let us consider a magnetic moment which, at time $t = 0$, is parallel to the field $\mathbf{B}_0$ (the case, for example, of a magnetic moment in thermodynamic equilibrium at very low temperatures : it is in the lowest energy state possible in the presence of the field $\mathbf{B}_0$). What happens when we apply a weak rotating field $\mathbf{B}_1(t)$? If the rotation frequency $\omega/2\pi$ of this field is very different from the natural frequency $\omega_0/2\pi$ (more precisely, if $\Delta\omega = \omega - \omega_0$ is much larger than ω_1), the effective field is directed practically along Oz. The precession of $\mathbf{m}(t)$ about $\mathbf{B}_{\text{eff}}$ then has a very small amplitude and hardly modifies the direction of the magnetic moment. On the other hand, if the resonance condition $\omega \simeq \omega_0$ is satisfied ($\Delta\omega \ll \omega_1$), the angle between the field $\mathbf{B}_{\text{eff}}$ and Oz is large. The precession of the magnetic moment then has a large amplitude and, at resonance ($\Delta\omega = 0$), the magnetic moment can even be completely flipped.

2. Quantum mechanical treatment

a. THE SCHRÖDINGER EQUATION

Let $|+\rangle$ and $|-\rangle$ be two eigenvectors of the projection S_z of the spin onto Oz, with respective eigenvalues $+\hbar/2$ and $-\hbar/2$. The state vector of the system can be written:

$$|\psi(t)\rangle = a_+(t)|+\rangle + a_-(t)|-\rangle \tag{11}$$

The Hamiltonian operator $H(t)$ of the system is*:

$$H(t) = -\mathbf{M}\,.\,\mathbf{B}(t) = -\gamma\,\mathbf{S}\,.\,[\mathbf{B}_0 + \mathbf{B}_1(t)] \tag{12}$$

that is, expanding the scalar product:

$$H(t) = \omega_0 S_z + \omega_1[\cos\omega t\, S_x + \sin\omega t\, S_y] \tag{13}$$

Using formulas (A-16) and (A-17) of chapter IV, we obtain the matrix which represents H in the $\{|+\rangle, |-\rangle\}$ basis:

$$H = \frac{\hbar}{2}\begin{pmatrix} \omega_0 & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & -\omega_0 \end{pmatrix} \tag{14}$$

Using (11) and (14), we can write the Schrödinger equation in the form:

$$\begin{cases} i\dfrac{d}{dt}a_+(t) = \dfrac{\omega_0}{2}a_+(t) + \dfrac{\omega_1}{2}e^{-i\omega t}a_-(t) \\ i\dfrac{d}{dt}a_-(t) = \dfrac{\omega_1}{2}e^{i\omega t}a_+(t) - \dfrac{\omega_0}{2}a_-(t) \end{cases} \tag{15}$$

b. CHANGING TO THE ROTATING FRAME

Equations (15) constitute a linear homogeneous system with time-dependent coefficients. It is convenient to define new functions by setting:

$$\begin{aligned} b_+(t) &= e^{i\omega t/2}a_+(t) \\ b_-(t) &= e^{-i\omega t/2}a_-(t) \end{aligned} \tag{16}$$

Substituting (16) into (15), we obtain a system which has constant coefficients:

$$\begin{cases} i\dfrac{d}{dt}b_+(t) = -\dfrac{\Delta\omega}{2}b_+(t) + \dfrac{\omega_1}{2}b_-(t) \\ i\dfrac{d}{dt}b_-(t) = \dfrac{\omega_1}{2}b_+(t) + \dfrac{\Delta\omega}{2}b_-(t) \end{cases} \tag{17}$$

* In expression (12), $\mathbf{M}\,.\,\mathbf{B}(t)$ symbolizes the scalar product $M_xB_x(t) + M_yB_y(t) + M_zB_z(t)$, where M_x, M_y and M_z are operators (observables of the system under study), while $B_x(t)$, $B_y(t)$ and $B_z(t)$ are numbers (since we consider the magnetic field to be a classical quantity whose value is imposed by an external device which is independent of the system under study).

This system can also be written:

$$i\hbar \frac{d}{dt} | \tilde{\psi}(t) \rangle = \tilde{H} | \tilde{\psi}(t) \rangle \tag{18}$$

if we introduce the ket $| \tilde{\psi}(t) \rangle$ and the operator $\tilde{H}$ defined by:

$$| \tilde{\psi}(t) \rangle = b_+(t) | + \rangle + b_-(t) | - \rangle \tag{19}$$

$$\tilde{H} = \frac{\hbar}{2} \begin{pmatrix} -\Delta\omega & \omega_1 \\ \omega_1 & \Delta\omega \end{pmatrix} \tag{20}$$

Transformation (16) has led to equation (18), which is analogous to a Schrödinger equation in which the operator $\tilde{H}$, given in (20), plays the role of a time-independent Hamiltonian. $\tilde{H}$ describes the interaction of the spin with a *fixed* field, whose components are none other than those of the effective field introduced above in the $OXYZ$ frame [formula (10)]. We can therefore consider that the transformation (16) is the quantum mechanical equivalent of the change from the fixed $Oxyz$ frame to the rotating $OXYZ$ frame.

This result can be proved rigorously. According to (16), we can write:

$$| \tilde{\psi}(t) \rangle = R(t) | \psi(t) \rangle \tag{21}$$

where $R(t)$ is the unitary operator defined by:

$$R(t) = e^{i\omega t S_z/\hbar} \tag{22}$$

We shall see later (*cf.* complement B_{VI}) that $R(t)$ describes a rotation of the coordinate system through an angle ωt about Oz. (18) is therefore indeed the transformed Schrödinger equation in the rotating $OXYZ$ frame.

Equation (18) is very simple to solve. To determine $| \tilde{\psi}(t) \rangle$, given $| \tilde{\psi}(0) \rangle$, all we need to do is expand $| \tilde{\psi}(0) \rangle$ on the eigenvectors of $\tilde{H}$ (which can be calculated exactly) and then apply rule (D-54) of chapter III (which is possible since $\tilde{H}$ is not explicitly time-dependent). We then go from $| \tilde{\psi}(t) \rangle$ to $| \psi(t) \rangle$ by using formulas (16).

c. TRANSITION PROBABILITY; RABI'S FORMULA

Consider a spin which, at time $t = 0$, is in the state $| + \rangle$:

$$| \psi(0) \rangle = | + \rangle \tag{23}$$

According to (16), this corresponds to:

$$| \tilde{\psi}(0) \rangle = | + \rangle \tag{24}$$

What is the probability $\mathcal{P}_{+-}(t)$ of finding this spin in the state $| - \rangle$ at time t? Since $a_-(t)$ and $b_-(t)$ have the same modulus, we can write:

$$\mathcal{P}_{+-}(t) = |\langle - | \psi(t) \rangle|^2 = |a_-(t)|^2 = |b_-(t)|^2 = |\langle - | \tilde{\psi}(t) \rangle|^2 \tag{25}$$

We must therefore calculate $|\langle - | \tilde{\psi}(t) \rangle|^2$, where $| \tilde{\psi}(t) \rangle$ is the solution of (18) which corresponds to the initial condition (24).

The problem we have just posed has already been solved, in § C-3-b of chapter IV. To use the calculations of that section, all we need to do is apply the following correspondences:

$$\begin{aligned} | \varphi_1 \rangle &\longrightarrow | + \rangle \\ | \varphi_2 \rangle &\longrightarrow | - \rangle \\ E_1 &\longrightarrow -\frac{\hbar}{2} \Delta\omega \\ E_2 &\longrightarrow \frac{\hbar}{2} \Delta\omega \\ W_{12} &\longrightarrow \frac{\hbar}{2} \omega_1 \end{aligned} \tag{26}$$

Rabi's formula [equation (C-32) of chapter IV] then becomes:

$$\mathcal{P}_{+-}(t) = \frac{\omega_1^2}{\omega_1^2 + (\Delta\omega)^2} \sin^2 \left[\sqrt{\omega_1^2 + (\Delta\omega)^2}\, \frac{t}{2} \right] \tag{27}$$

The probability $\mathcal{P}_{+-}(t)$ is, of course, zero at time $t = 0$ and then varies sinusoidally with respect to time between the values 0 and $\dfrac{\omega_1^2}{\omega_1^2 + (\Delta\omega)^2}$. Again, we have a resonance phenomenon. For $|\Delta\omega| \gg |\omega_1|$, $\mathcal{P}_{+-}(t)$ remains almost zero (*cf.* fig. 3-a); near resonance, the oscillation amplitude of $\mathcal{P}_{+-}(t)$ becomes large and, when the condition $\Delta\omega = 0$ is exactly satisfied, we have $\mathcal{P}_{+-}(t) = 1$ at times $t = \dfrac{(2n+1)\pi}{\omega_1}$ (*cf.* fig. 3-b).

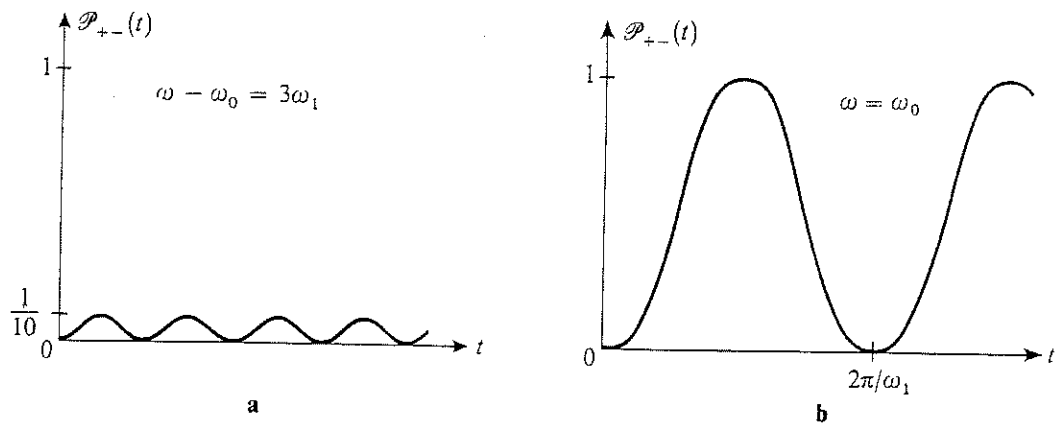

FIGURE 3

Variation with respect to time of the transition probability between the states $| + \rangle$ and $| - \rangle$, under the effect of a rotating magnetic field $B_1(t)$. Outside resonance (fig. a), this probability remains small; at resonance (fig. b), however small the field B_1, there exist times when the transition probability is equal to 1.

Thus we again find the result which we have already obtained classically : at resonance, a very weak rotating field is able to reverse the direction of the spin. Note, moreover, that the angular frequency of the oscillation of $\mathscr{P}_{+-}(t)$ is $\sqrt{\omega_1^2 + (\Delta\omega)^2} = |\gamma \mathbf{B}_{eff}|$. This oscillation corresponds, in the rotating frame, to the projection onto OZ of the precession of the magnetic moment about the effective field, sometimes called "Rabi precession" [see also the calculation of $\mathscr{P}_{+-}(t)$ in complement C_{IV}, § 3-c].

d. CASE WHERE THE TWO LEVELS ARE UNSTABLE

We are now going to assume that the two states $|\pm\rangle$ correspond to two sublevels of an excited atomic level (whose angular momentum is assumed equal to 1/2). n atoms are excited per unit time, all being raised to the state $|+\rangle$*. An atom decays, by spontaneous emission of radiation, with a probability per unit time of $1/\tau$, which is the same for the two sublevels $|\pm\rangle$. We know that, under these conditions, an atom which was excited at time $-t$ has a probability $e^{-t/\tau}$ of still being excited at time $t = 0$ (*cf.* complement K_{III}).

We assume that the experiment is performed in the steady state : in the presence of the fields $\mathbf{B}_0$ and $\mathbf{B}_1(t)$, the atoms are excited at a constant rate n into the state $|+\rangle$. After a time much longer than the lifetime τ, what is the number N of atoms which decay per unit time from the state $|-\rangle$? If an atom is excited at time $-t$, the probability of finding it in the state $|-\rangle$ at $t = 0$ is $e^{-t/\tau}\mathscr{P}_{+-}(t)$, where $\mathscr{P}_{+-}(t)$ is given by relation (27). The total number of atoms in the state $|-\rangle$ is obtained by taking the sum of atoms excited at all previous times $-t$, that is, by calculating the integral:

$$\int_0^\infty e^{-t/\tau}\,\mathscr{P}_{+-}(t)\,n\,dt \tag{28}$$

This calculation presents no difficulties. Multiplying the number of atoms thus obtained by their probability $1/\tau$ of decay per unit time, we obtain:

$$N = \frac{n}{2}\,\frac{\omega_1^2}{(\Delta\omega)^2 + \omega_1^2 + (1/\tau)^2} \tag{29}$$

The variation of N with respect to $\Delta\omega$ corresponds to a Lorentz curve whose half-width is:

$$L = \sqrt{\omega_1^2 + (1/\tau)^2} \tag{30}$$

In the experiment described above, let us measure, for various values of the magnetic field B_0 (that is, with ω assumed to be fixed, for various values of $\Delta\omega$), the number of atoms which decay from the level $|-\rangle$. According to (29), we obtain a resonance curve which has the shape shown in figure 4.

It is very interesting to obtain such a curve experimentally, since one can use it to determine several parameters:

– if we know ω and measure the value B_0^m of the field B_0 which corresponds to the peak of the curve, we can deduce the value of the gyromagnetic ratio γ through the relation $\gamma = -\omega/B_0^m$.

* In practice, this excitation can be produced, for example, by placing the atoms in a light beam. When the incident photons are polarized, conservation of angular momentum, in certain cases, requires that the atoms which absorb them can attain only the state $|+\rangle$ (and not the state $|-\rangle$). Similarly, by detecting the polarization of the photons re-emitted by the atoms, one can know whether the atoms fall back into the ground state from the state $|+\rangle$ or the state $|-\rangle$.

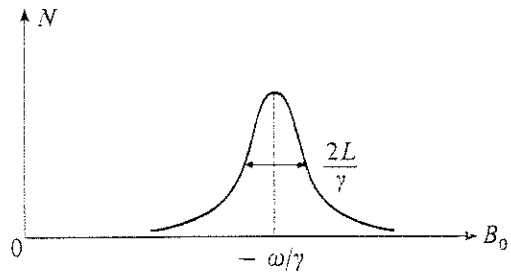

FIGURE 4

Resonance curve. To observe a resonance phenomenon, we perform an experiment in which n atoms are excited per unit time into the state $|+\rangle$. Under the effect of a field $B_1(t)$, rotating at the frequency $\omega/2\pi$, the atoms undergo transitions towards the state $|-\rangle$. In the steady state, if we measure the number N of atoms which decay per unit time from the state $|-\rangle$, we obtain a resonant variation when we scan the static field B_0 about the value $-\omega/\gamma$.

– if we know γ, we can, by measuring the frequency $\omega/2\pi$ which corresponds to resonance, measure the static magnetic field B_0. Various magnetometers, often of very great precision, operate on this principle. In certain cases, one can derive interesting information from such a measurement of the field. If, for example, the spin being considered is that of a nucleus which belongs to a molecule or to a crystal lattice, one can find the local field seen by the nucleus, its variation with the site occupied, etc.

– if we trace the square L^2 of the half-width as a function of ω_1^2, we obtain a straight line which, extrapolated to $\omega_1 = 0$, gives the lifetime τ of the excited level (*cf.* fig. 5).

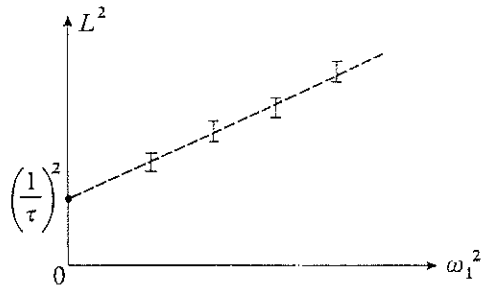

FIGURE 5

The extrapolation to $\omega_1 = 0$ of the squared half-width L of the resonance curve of figure 4 gives the lifetime of the level being studied.

3. Relation between the classical treatment and the quantum mechanical treatment: evolution of $\langle \mathbf{M} \rangle$

The results obtained in §§1 and 2 are very similar, although we used classical mechanics in one case and quantum mechanics in the other. We are now going to show that this similarity is not accidental. It arises from the fact that the quantum mechanical evolution equations of the mean value of a magnetic moment placed in an arbitrary magnetic field are identical to the corresponding classical equations.

The mean value of the magnetic moment associated with a spin 1/2 is:

$$\langle \mathbf{M} \rangle(t) = \gamma \langle \mathbf{S} \rangle(t) \tag{31}$$

To calculate the evolution of $\langle \mathbf{M} \rangle(t)$, we use theorem (D-27) of chapter III:

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \langle \mathbf{M} \rangle(t) = \langle [\mathbf{M}, H(t)] \rangle \tag{32}$$

where $H(t)$ is the operator:

$$H(t) = -\mathbf{M} \cdot \mathbf{B}(t) \tag{33}$$

Let us calculate for example the commutator $[M_x, H(t)]$. Using the fact that the field components $B_y(t)$ and $B_z(t)$ are numbers (*cf.* note of §2-a), we find:

$$\begin{aligned}[M_x, H(t)] &= -\gamma^2[S_x, S_xB_x(t) + S_yB_y(t) + S_zB_z(t)] \\ &= -\gamma^2 B_y(t)[S_x, S_y] - \gamma^2 B_z(t)[S_x, S_z]\end{aligned} \tag{34}$$

Using relations (14) of complement A_{IV}, we obtain:

$$[M_x, H(t)] = i\hbar\gamma^2[B_z(t)S_y - B_y(t)S_z] \tag{35}$$

Substituting (35) into (32):

$$\frac{d}{dt}\langle M_x \rangle(t) = \gamma[B_z(t)\langle M_y \rangle(t) - B_y(t)\langle M_z \rangle(t)] \tag{36}$$

By cyclic permutation, we can calculate analogous expressions for the components on Oy and Oz; the three equations obtained can be condensed into:

$$\frac{d}{dt}\langle \mathbf{M} \rangle(t) = \gamma \langle \mathbf{M} \rangle(t) \times \mathbf{B}(t) \tag{37}$$

Let us compare (37) with (6): the evolution of the mean value $\langle \mathbf{M} \rangle(t)$ obeys the classical equations exactly, whatever the time-dependence of the magnetic field $\mathbf{B}(t)$.

4. Bloch's equations

In practice, in a magnetic resonance experiment, it is not the magnetic moment of a single spin that is observed, but rather that of a great number of identical spins (as in the experiment described in §2-d above, where the number of atoms which decay from the state $|-\rangle$ is detected). Moreover, one is not concerned solely with the quantity $\mathcal{P}_{+-}(t)$, calculated above. One can also measure the global magnetization $\mathcal{M}$ of the sample under study: the sum of the mean values of the observable $\langle \mathbf{M} \rangle$ corresponding to each spin of the sample*. It is interesting, therefore, to obtain the equations of motion of $\mathcal{M}$, called the *Bloch equations*.

In order to understand the physical significance of the various terms appearing in these equations, we are going to derive them for a simple concrete case. The results obtained can be generalized to other more complicated situations.

a. A CONCRETE EXAMPLE

Consider a beam of atoms issuing from an atomic polarizer of the type studied in §B-1-a of chapter IV. All the atoms of the beam** are in the spin state $|+\rangle$ and therefore have their magnetic moments parallel to Oz. They enter a cell C through a small opening (fig. 6), rebound a certain number of times from the inside walls of the cell and, after a certain time, escape through the same opening.

* It is possible to detect, for example, the electromotive force emf induced in a coil by the variation of $\mathcal{M}$ with respect to time.

** For example, silver or hydrogen atoms in the ground state. For the sake of simplicity, all effects related to nuclear spin are neglected.

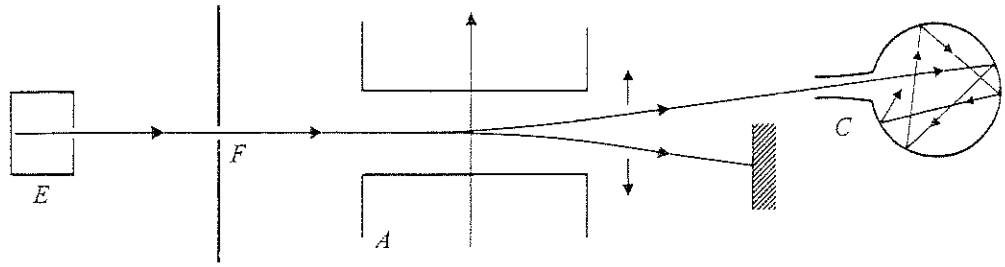

FIGURE 6

Schematic drawing of an experimental device which supplies cell C with atoms in the state $|+\rangle$.

We shall denote by n the number of polarized atoms entering the cell per unit time; n is generally small and the atomic density inside the cell is low enough to allow atomic interactions to be neglected. Moreover, if the inside walls of the cell are suitably coated, collisions with the walls have little effect on the spin state of the atoms*. We shall assume that there is a probability per unit time $1/T_R$ for the elementary magnetization introduced into the cell by a polarized atom to disappear, either because of a depolarizing collision with the walls or simply because the atom has left the cell. T_R is called the "relaxation time". The cell is placed in a magnetic field $\mathbf{B}(t)$ which may have a static component and a rotating component. The problem consists of finding the equation of motion of the global magnetization $\mathcal{M}(t)$ of the atoms which are inside the cell at time t. First, let us write the exact expression for $\mathcal{M}(t)$:

$$\mathcal{M}(t) = \sum_{i=1}^{\mathcal{N}} \langle \psi^{(i)}(t) | \mathbf{M} | \psi^{(i)}(t) \rangle = \sum_{i=1}^{\mathcal{N}} \mathcal{M}^{(i)}(t) \tag{38}$$

In (38), the sum is taken over the $\mathcal{N}$ spins which are already in the cell and which, at time t, have neither left nor undergone a depolarizing collision. $|\psi^{(i)}(t)\rangle$ is the state vector of such a spin (i) at time t [we are not counting, in (38), the spins which have undergone a depolarizing collision and have not yet left the cell, since their global contribution is zero: their spins point randomly in all directions].

Between times t and $t + dt$, $\mathcal{M}(t)$ varies for three different reasons:

(i) A certain proportion, dt/T_R, of the $\mathcal{N}$ spins undergo a depolarizing collision or leave the compartment; these spins disappear from the sum (38) and $\mathcal{M}(t)$ therefore decreases by:

$$d\mathcal{M}(t) = -\frac{dt}{T_R}\mathcal{M}(t) \tag{39}$$

(ii) The other spins evolve freely in the field $\mathbf{B}(t)$. We saw in § 3 above that, for each of them, the evolution of the mean value of $\mathbf{M}$:

$$\mathcal{M}^{(i)}(t) = \langle \psi^{(i)}(t) | \mathbf{M} | \psi^{(i)}(t) \rangle$$

obeys the classical law:

$$d\mathcal{M}^{(i)}(t) = \gamma \mathcal{M}^{(i)}(t) \times \mathbf{B}(t)\, dt \tag{40}$$

Since the right-hand side of (40) is linear with respect to $\mathcal{M}^{(i)}(t)$, the contribution of these spins to the variation of $\mathcal{M}(t)$ is given by:

$$d\mathcal{M}(t) = \gamma \mathcal{M}(t) \times \mathbf{B}(t)\, dt \tag{41}$$

* For example, for hydrogen atoms bouncing off teflon walls, tens of thousands of collisions are required for the magnetic moment of the hydrogen atom to become disoriented.

(*iii*) Finally, a certain number, $n\,dt$, of new spins have entered the cell. Each of them adds to the global magnetization a contribution $\boldsymbol{\mu}_0$, equal to the mean value of $\mathbf{M}$ in the state $|+\rangle$ ($\boldsymbol{\mu}_0$ is parallel to Oz and $|\boldsymbol{\mu}_0| = |\gamma|\frac{\hbar}{2}$). $\mathcal{M}$ therefore increases by:

$$d\mathcal{M}(t) = n\,\boldsymbol{\mu}_0\,dt \tag{42}$$

The global variation of $\mathcal{M}$ is obtained by adding (39), (41) and (42). Dividing by dt, we obtain the equation of motion of $\mathcal{M}(t)$ (Bloch equation):

$$\frac{d}{dt}\mathcal{M}(t) = n\,\boldsymbol{\mu}_0 - \frac{1}{T_R}\mathcal{M}(t) + \gamma\mathcal{M}(t)\times\mathbf{B}(t) \tag{43}$$

We have derived (43) in a specific case, making certain hypotheses. However, the main features of this equation remain valid for a great number of other experiments where the rate of variation of $\mathcal{M}(t)$ appears in the form of a sum of three terms:

– a source term (here $n\,\boldsymbol{\mu}_0$) which describes the preparation of the system. It would, in fact, be impossible to observe magnetic resonance without a preliminary polarization of the spins, which can be achieved through selection using a magnetic field gradient (as in the example studied here), a polarized optical excitation (as in the example studied in § 2-d above), cooling of the sample in a strong static field, etc.

– a damping term $\left(\text{here } -\frac{1}{T_R}\mathcal{M}(t)\right)$ which describes the disappearance or "relaxation" of the global magnetization under the effect of various processes : collisions, disappearance of atoms, change in atomic levels through spontaneous emission (as in the example studied in § 2-d), etc.

– a term which describes the precession of $\mathcal{M}(t)$ in the field $\mathbf{B}(t)$ [last term of (43)].

b. SOLUTION IN THE CASE OF A ROTATING FIELD

When the field $\mathbf{B}(t)$ is the sum of a static field $\mathbf{B}_0$ and a rotating field $\mathbf{B}_1(t)$, such as those considered above, equations (43) can be solved exactly. As in §§ 1 and 2, one changes to the rotating frame $OXYZ$, with respect to which the relative variation of $\mathcal{M}(t)$ is:

$$\left(\frac{d}{dt}\mathcal{M}\right)_{\text{rel}} = n\,\boldsymbol{\mu}_0 - \frac{1}{T_R}\mathcal{M} + \gamma\mathcal{M}\times\mathbf{B}_{\text{eff}} \tag{44}$$

[where $\mathbf{B}_{\text{eff}}$ is defined by equation (10)].

Projecting this equation onto OX, OY and OZ, we obtain a system of three linear differential equations with constant coefficients whose stationary solution (valid after a time much greater than T_R) is:

$$\begin{aligned}
(\mathcal{M}_X)_S &= -\,n\mu_0 T_R\,\frac{\omega_1\,\Delta\omega}{(\Delta\omega)^2 + \omega_1^2 + (1/T_R)^2} \\
(\mathcal{M}_Y)_S &= -\,n\mu_0\,\frac{\omega_1}{(\Delta\omega)^2 + \omega_1^2 + (1/T_R)^2} \\
(\mathcal{M}_Z)_S &= n\mu_0 T_R\left[1 - \frac{\omega_1^2}{(\Delta\omega)^2 + \omega_1^2 + (1/T_R)^2}\right]
\end{aligned} \tag{45}$$

The three components of the stationary magnetization $(\mathcal{M})_S$, when the field B_0 varies, have resonant variations about the value $B_0 = -\omega/\gamma$ (*cf.* fig. 7). $(\mathcal{M}_Y)_S$ and $(\mathcal{M}_Z)_S$ give absorption curves $\left(\text{Lorentz curves of width } \frac{2}{\gamma}\sqrt{\omega_1^2 + (1/T_R)^2}\right)$. $(\mathcal{M}_X)_S$ gives a dispersion curve (of the same width).

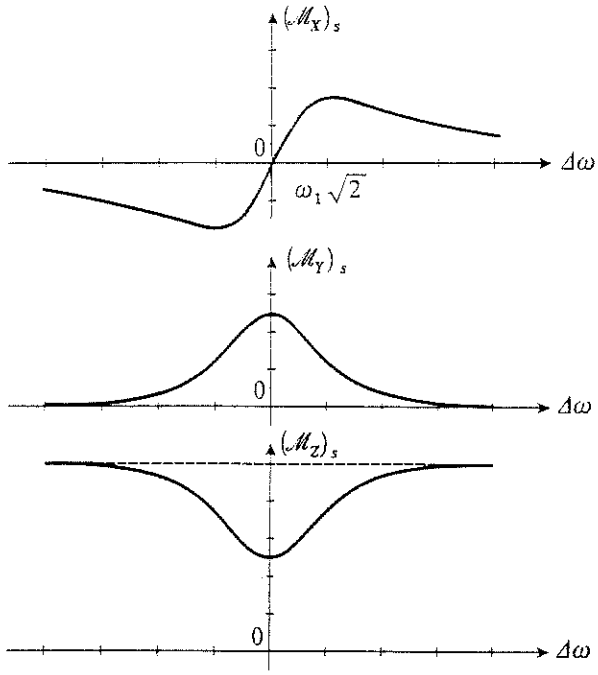

FIGURE 7

Variation with respect to $\Delta\omega = \omega - \omega_0$ of the stationary values of the components of $\mathcal{M}$ in the rotating frame. One obtains a dispersion curve for $(\mathcal{M}_X)_S$ and absorption curves for $(\mathcal{M}_Y)_S$ and $(\mathcal{M}_Z)_S$. The three curves have the same width, $2\sqrt{\omega_1^2 + (1/T_R)^2}$, which increases with ω_1. They have been drawn assuming that $\omega_1 = 1/T_R$ ("half-saturation").

The comments made at the end of § 2-d above about the experimental interest of such curves can be repeated here.

References and suggestions for further reading:

Feynman II (7.2), chap. 35; Cagnac and Pebay-Peyroula (11.2), chaps. IX § 5, X § 5, XI §§ 2 to 5, XIX § 3; Kuhn (11.1), § VI, D.

See the references of section 14 of the bibliography, particularly Abragam (14.1) and Slichter (14.2).