Pre-requisites: A course in quantum mechanics, at the intermediate level, is required for a decent understanding of the material here. Readers or auditors without this background will find difficult going. Beyond this, a good course in linear algebra, and some familiarity with the Bloch equations are needed.

A few introductory remarks: the theory of quantum angular momentum is closely tied to the quantum theory of rotations (*1, 2*). That is, an angular momentum operator, e.g. L_z, represents an infinitesimal rotation about the *z* axis of a chosen coordinate system. A rotation of finite magnitude can be considered the composition of many infinitesimal rotations; mathematically this is expressed by complex exponentiation of the angular momentum operator.

For an electron, we distinguish between orbital angular momentum, arising from the trajectory of its center of mass, and spin angular momentum, associated with no particular motion, but which is an intrinsic property of the electron itself (*3).* Certain nuclei also possess spin, rendering them susceptible to study by magnetic resonance.

The quantization of orbital angular momentum for atomic electrons is described by spherical harmonics, whose order - written conventionally as l-- takes the values of all positive integers, starting with 0. The square of the angular momentum l is given by $l(l+1)$, and the *z* component takes the values $m = l, l-1, l-2, \ldots -l$, that is, descending in steps of unity.

Although the discovery of spin angular momentum is tied to atomic spectroscopy, the famous Stern Gerlach experiment (*4*) affords the clearest illustration of its existence. Passage of a beam of atomic hydrogen, in its ground state, through an inhomogeneous magnetic field, gives a pair of spots on a detection screen, due to splitting of beam by the magnetic moment of hydrogen. Since the unpaired 1s electron of hydrogen has zero orbital angular momentum, the moment must be ascribed to an intrinsic angular momentum of the electron, which we now call spin. The presence of a pair of dots, suggests that the two components of *z*-directed angular momentum, must have the values $\pm 1/2$, by analogy with orbital momentum, which dictates that the decrement should be unity. In Dirac bracket notation (5), the spin states corresponding to the two detected dots are represented the kets (so called) $|\alpha\rangle$ and $|\beta\rangle$. In Hilbert space these may be written as two-vectors:

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ and } |\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

These two-component vectors are also referred to as spinors, and are the state vectors for the spin component of particles of spin 1/2.

As an aside, the original Stern-Gerlach experiment was done with atomic silver, whose presence was undetectable until examination of the dis-assembled apparatus by Stern (a smoker of cheap cigars) revealed two black dots of silver sulfide, formed by the hydrogen sulfide in the smoke on his breath.

Certain nuclei also possess the property of spin, particularly the proton, a particle of spin 1/2 with which we are particularly concerned. Nuclear spin was also discovered via atomic spectroscopy, but its clearest demonstration was through the Rabi molecular beam experiments (*6*), which combine features of the Stern-Gerlach experiment with the radiofrequency methods that have come to be common in magnetic resonance. Unfortunately we have not space for a detailed treatment.

Then we seek a set of Hermitian operators, acting upon the spinors, to describe a particle of spin 1/2; these will be of dimension two, over the field of complex numbers, and we arrive at the familiar Pauli matrices:

$$\boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \text{ and } \boldsymbol{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

is readily seen that any 2x2 Hermitian matrix can be formed as a real linear combination of the Pauli matrices plus the identity matrix. Note that the two spinors $|\alpha\rangle$ and $|\beta\rangle$ are eigenvectors of $\boldsymbol{\sigma}_z$, with eigenvalues ± 1. The Pauli matrices are then converted into the spin operators S_x, S_y, and S_z, by the simple expedient of scalar multiplication by 1/2. Thus we get

$$S_x = (1/2)\boldsymbol{\sigma}_x, \qquad S_y = (1/2)\boldsymbol{\sigma}_y, \qquad S_z = (1/2)\boldsymbol{\sigma}_z.$$

When the Pauli matrices are so multiplied the eigenvalues of the spinors become $\pm 1/2$.

The eigenvalues for the other Pauli matrices, $\boldsymbol{\sigma}_x$ and $\boldsymbol{\sigma}_y$, may be gotten by direct calculation, but we will prefer quantum rotation, as a more difficult, but more educational means for obtaining these. Our approach is intuitive and heuristic. Inasmuch as the to two spinors $|\alpha\rangle$ and $|\beta\rangle$ represent spins with oppositely polarized z components, we surmise that their sum, the normalized linear combination $(1/\sqrt{2})(|\alpha\rangle + |\beta\rangle)$ could represent a spin tipped by an angle of $\pi/2$ and lying along the *x* axis of a chosen coordinate system. We then seek a rotation matrix $\mathbf{R}$ that would perform this operation:

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

This leads immediately to:

$$\begin{bmatrix} a_{11} \\ a_{21} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \text{ whence, by unitarity, } \begin{bmatrix} a_{12} \\ a_{22} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 \\ 1 \end{bmatrix};$$

that is, $\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} = \mathbf{1}\cos\frac{\pi}{4} - i\sin\frac{\pi}{4}\boldsymbol{\sigma}_y$ where $\mathbf{1}$ is the unit matrix of dimension two. The reader may verify that the vectors resulting from multiplication by this matrix of $|\alpha\rangle$ and $|\beta\rangle$ are in fact the eigenvectors of $\boldsymbol{\sigma}_x$, with eigenvalues ± 1. We then postulate the matrix for a rotation about *y* of an arbitrary angle: $\exp(-i\frac{\vartheta}{2}\boldsymbol{\sigma}_y) = \mathbf{1}\cos\frac{\vartheta}{2} - i\sin\frac{\vartheta}{2}\boldsymbol{\sigma}_y$, and by extension, for rotation about *x* as

$\exp(-i\frac{\vartheta}{2}\boldsymbol{\sigma}_x) = \mathbf{1}\cos\frac{\vartheta}{2} - i\sin\frac{\vartheta}{2}\boldsymbol{\sigma}_x$. Then clearly, rotation through ϑ about an arbitrary axis $\mathbf{n}$ whose direction cosines are $\begin{bmatrix} n_x & n_y & n_z \end{bmatrix}$ is given by $\mathbf{1}\cos\frac{\vartheta}{2} - i\sin\frac{\vartheta}{2}\mathbf{n}\bullet\boldsymbol{\sigma}$, where the dot product is of $\mathbf{n}$ with a vector comprising the three Pauli matrices. Although we will not explain the details, the half-angles in the rotation matrices arise from the multiplier of $1/2$ introduced above.

With the rotation matrices in hand, we now demonstrate interconvertibility of the Pauli matrices are by unitary transformation. For example, for a rotation of $\boldsymbol{\sigma}_z$ by an angle $\pi/2$ about the *y* axis, we have, using the transformation matrix above:

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

That is: $\boldsymbol{\sigma}_x = \mathbf{R}\boldsymbol{\sigma}_z\mathbf{R}^{-1}$, by the usual machinery of similarity (in this instance unitary) transformation. For a general rotation of $\boldsymbol{\sigma}_z$ about *y*, using the transformation matrix $\exp(-i\frac{\vartheta}{2}\boldsymbol{\sigma}_x)$ given above, we get:

$$\exp(-i\frac{\vartheta}{2}\boldsymbol{\sigma}_x)\boldsymbol{\sigma}_z\exp(i\frac{\vartheta}{2}\boldsymbol{\sigma}_x) = \boldsymbol{\sigma}_z[\cos^2\frac{\vartheta}{2} - \sin^2\frac{\vartheta}{2}] + 2\boldsymbol{\sigma}_x\cos\frac{\vartheta}{2}\sin\frac{\vartheta}{2}$$

$$= \boldsymbol{\sigma}_z\cos\vartheta + \boldsymbol{\sigma}_x\sin\vartheta$$

that is, the half angles disappear and the result is exactly similar to that obtained for rotation of a *z*-directed unit vector through the same angle about the *y* axis.

The reader will easily supply examples, to further illustrate what we have shown--namely that the Pauli matrices transform among themselves like vector components; in particular, the troublesome half-angles, present in the transformation of spinors, now disappear.

Now in general, the vector nuclear magnetic moment for a nucleus of spin 1/2 may be written in operator form as a linear combination of Pauli matrices:

$$\boldsymbol{\mu} = \tfrac{1}{2}\gamma\hbar\sum_{1=1}^{3} n_i\mathbf{e}_i\boldsymbol{\sigma}_i$$

where the n_i's are direction cosines, the $\mathbf{e}_i$'s are unit vectors, γ is the gyromagnetic ratio, and we have used the usual reduced Planck constant.
Note that we have here placed the essential factor of 1/2 outside the summation.

This quantum expression for the nuclear magnetic moment provides a link to the classical Bloch equations (*7, 8*), which describe the motion of the nuclear magnetization, i.e. the magnetic moment per unit volume. Given the widespread use of the Bloch equations for classical calculations of NMR dynamics, we may safely assert that all practical quantum mechanical computations of spin dynamics are best performed with the magnetic moment and Pauli matrices, rather than with spinors.

We now consider briefly how practical rotations are produced in the laboratory. Starting with the expression for the energy of a magnetic moment in a ~~uniform~~ magnetic field, $E=-\mu\bullet\mathbf{B}$, we stipulate that B comprises a static component directed along the *z* axis, and an oscillatory component along *x*. Confining our attention to the interaction with oscillatory field, which we call B_{RF}, we write: $E_{RF}=-\mu_x B_{RF}\cos\omega t$, where the cosine term contains the angular frequency of the oscillatory field. Note the presence of a Pauli matrix means that this expression, considered as a quantum operator, is the generator of an infinitesimal rotation.

This term is usually treated semi-classically, i.e. by writing the magnetic moment quantum mechanically (as above) in terms of the appropriate Pauli matrices, and leaving the field in its classical form. The lack of a fully quantum mechanical treatment -- which should include both spins and field-- is hindered by the difficulty of quantizing what is called the 'near', as opposed to the 'far' or 'radiation' field. However, recent work (*9*) has shown how a fully quantum mechanical treatment is possible, quantizing not the field, but the LC oscillator comprising the NMR probe, or antenna. Time permitting, a brief discussion of this work may be presented. One difficulty arises in that the fully quantum mechanical operator is no longer a generator of an infinitesimal rotation, even though the spins do rotate under its influence.

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