

# Pairs of two-level systems

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Correlations between the orientations of two particles with spin  $\frac{1}{2}$  are formulated in terms of a complete set of operators appropriate to display the spectrum of oscillations under the influence of the spin interactions. The operators are classified for this purpose according to space and permutation symmetries. The treatment is intended as a model for any pair of two-level systems. Its extension to multilevel systems and the eventual emergence of dissipative behavior are outlined. The correlation of two-photon polarizations in the Einstein-Rosen-Podolsky paradox is described as an illustration.

## CONTENTS

I. Introduction	855
II. Development of Formalism: The Orientation of Particles with Spin $\frac{1}{2}$	856
A. Pure states	856
B. Representation of partial polarization	857
C. Time dependence	857
D. State of thermal equilibrium	858
E. Two-level systems	859
III. Electron-Proton Spin Correlations	859
A. Base set of operator products	859
B. Symmetrized operators and state parameters	861
C. Time dependence and scattering	862
D. Conservation law	864
E. Reversibility and its practical limits	864
F. Vanishing of polarization components through symmetry	865
G. Time dependence with a nondegenerate spectrum	865
H. Summary	867
IV. Correlations in States with Zero Net Spin	867
A. Stationary state with spin quantum number $F=0$	867
B. Stationary state with $F=1$ and $M=0$	868
C. Correlation of photon pairs	868
V. Extensions	869
A. Parameters of spin- $j$ states	870
B. Mapping of $N$ -level systems and of correlated subsystems	870
C. Observation of time-dependent correlations	871
D. Correlations in large systems and their dissipation	872
Acknowledgments	873
References	873

## I. INTRODUCTION

The remark by Feynman *et al.* (1957) that the orientation of a particle with spin  $\frac{1}{2}$  affords a model for the quantum mechanics of all two-level systems has proved extremely influential. Many of the concepts and much of the language of quantum optics, for example, stem from that remark, even though their origin has now receded in the background. The complementary development of the two-level treatment in density matrix language (Fano, 1957) has also been influential by providing simple illustrations of the interface of quantum mechanics with both classical and statistical mechanics.

This article extends the same approach to systems consisting of two (or more) particles—even of molecular or macroscopic aggregates—whose physics depends critically on correlated particle motions. For example, the rich

field of magnetic resonance studies depends on correlations between the spin orientations of neighbor particles. “Correlation” is a general term which refers in statistics to the mean (or “expectation”) value of the product of two different variables. More specifically, one calls correlation the departure of the mean product of two variables, e.g., of two coordinates  $x$  and  $y$ , from the product of their separate mean values

$$\langle xy \rangle - \langle x \rangle \langle y \rangle. \quad (1.1)$$

The evaluation of such mean values for any specific case is in principle a familiar task of quantum mechanics. However, performing this task correctly and transparently requires some skill as well as care in formulating each problem. The same holds when applying probability theory in classical physics.

As a prototype I consider here correlations between the orientations of two particles with spin  $\frac{1}{2}$ . More specifically, I shall describe the statistical distribution of the spin orientations of particles brought together initially in a fixed orientation, e.g., one with “spin up” and one with “spin down.” Interactions change these orientations in the course of time, thus inducing correlations. Fourier analysis of the time dependence of these correlations displays the eigenfrequency spectrum of the pair. As for a single particle, our treatment of a pair of spins will be equally applicable to any pair of two-level systems, typically to pairs of light polarizations. The adaptation of the treatment to the orientation (or alignment) of higher spins will also be indicated. Note that the treatment of spin orientations is viewed as the prototype for all of quantum physics in Vol. III of Feynman’s *Lectures on Physics* (1965) and in Chaps. 8–10 of Fano and Fano (1972). We shall thus be dealing with schematic problems of simple systems with an eye to their relevance to more general phenomena.

Striking and famous examples of correlations occur when two particles or photons emerge from the fragmentation of a system isotropic in space. The decay of spinless parapositronium thus yields a photon pair such that the separate polarization of each photon is necessarily random—corresponding to  $\langle x \rangle = 0$  and  $\langle y \rangle = 0$  in (1.1)—but is nevertheless tightly correlated to those of the other photon, whereby  $\langle xy \rangle \neq 0$ . This quantum phenomenon has been discussed widely as the Einstein-Rosen-Podolsky paradox and will be described in Sec. IV.

It may seem strange that the study of a simple pair of

spins should provide guidance for the treatment of very complicated systems. In fact, however, physics problems deal normally with a modest number of independent observables. In the extreme case of thermal equilibrium the state of a system is identified by a single parameter, the temperature. Additional parameters of interest will be the mean values of the operators coupled to the fields of a specific experiment. This article will show how parameters of a complex system independent of those under study would actually be set to zero by symmetry arguments in a fully detailed statement of the problem, though this circumstance is seldom stated explicitly.

Let us consider also that the parameters of actual interest in a complex system are generally mean values of operators characterized as "collective variables." For example, a long-wave oscillating electric field couples to the electric polarization of a material, that is, to the displacement of the center of mass of all electrons from the center of charge of all nuclei. This displacement is the collective variable of interest. The treatment of simple examples in this article is intended to guide the selection of variables that are independent of the parameters of interest and whose mean values are properly set to zero.

To be a little more specific, we can recall that the mean value of an operator (or product of operators in the case of correlations) depends of course on the state of any given system. Conversely, the state itself is identified by the mean values of a sufficient set of the system's variables. The task of calculating mean values is thus largely equivalent to the task of *characterizing any state by a suitable set of parameters*. While the number of parameters required to identify the state of a system will be seen to increase exponentially with the number of its particles, most of them may be so chosen as to vanish identically, as noted above. In our simple spin systems this vanishing merely reflects trivial considerations of symmetry. The study of a spin pair will be conducted so as to guide the reader in extending symmetry elements to the analysis of more complex systems.

Fifteen parameters are required to identify the orientation state of the simple pair of spin  $\frac{1}{2}$ , as we shall see; this number increases dramatically for larger systems. Achieving an overview of such large sets requires a suitable classification scheme. The description of a classification based on space and permutation symmetries forms the core of this article. The classification will also facilitate the analysis of the time dependence of the parameters of interest. Further, it will be made applicable to systems with lower symmetries by the artifice of mapping their eigenstates and operators onto those of more symmetric systems.

The physical concepts and analytical techniques to be employed originate from the density matrix treatment of a single spin (Fano, 1957). That treatment is reviewed in Sec. II to make this article self-contained. Section III forms the core of the article, dealing explicitly with a pair of two-level systems. Section IV describes the correlations of two spins or photon polarizations originating from the decay of an isotropic source. Section V intro-

duces extensions to larger systems, whose treatment might utilize the concepts and techniques developed for simple examples.

## II. DEVELOPMENT OF FORMALISM: THE ORIENTATION OF PARTICLES WITH SPIN $\frac{1}{2}$

The spin orientation of particles in a beam may be observed by filtration through a Stern-Gerlach device, which resolves the beam into two components with "spin up" and "down," respectively. The main output of this analysis consists of the ratio

$$P = \frac{I_+ - I_-}{I_+ + I_-}, \quad (2.1)$$

where  $I_+$  ( $I_-$ ) indicates the intensity of the spin-up (-down) component of the beam. The observed value of  $P$  depends, of course, on the direction of the magnetic field within the Stern-Gerlach device; by varying the orientation of this device one determines the field direction for which  $P$  is largest. This *maximum value* of  $P$  is defined as the beam *polarization* and is represented as a vector  $\mathbf{P}$  parallel to the field orientation that maximizes  $P$ . Equivalent procedures serve to determine  $\mathbf{P}$  for sets of particles that are, for example, dispersed in a medium instead of being assembled in a beam. Note that  $P$ , as defined by (2.1), ranges from  $-1$  to  $1$ , while the resulting magnitude of the polarization vector,  $P = |\mathbf{P}|$ , ranges from  $0$  to  $1$ .

### A. Pure states

Analytically a pure state of a spin- $\frac{1}{2}$  particle is represented by a two-component spinor

$$\psi_m(\theta, \phi) = \frac{1}{2} \begin{matrix} m \\ \exp(-i\frac{1}{2}\phi)\cos\frac{1}{2}\theta \\ -\frac{1}{2} \exp(+i\frac{1}{2}\phi)\sin\frac{1}{2}\theta \end{matrix}. \quad (2.2)$$

A measurement of the polarization  $\mathbf{P}$ , as defined above, amounts to an experimental determination of the expectation value  $\langle \sigma \rangle$  of the Pauli spin operator

$$\sigma \equiv \{ \sigma_x, \sigma_y, \sigma_z \}, \quad (2.3)$$

whose components have the eigenvalues  $\pm 1$ . Theoretical calculation of

$$\langle \sigma \rangle \equiv \mathbf{P} \quad (2.4)$$

for the state represented by the spinor (2.2), using the standard matrix representation,

$$\sigma_x = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad \sigma_y = \begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix}, \quad \sigma_z = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}, \quad (2.5)$$

yields a vector  $\mathbf{P}$  of unit magnitude and of direction  $(\theta, \phi)$ . This result means that states represented by (2.2) are characterized by unit polarization and interprets the parameters  $\theta$  and  $\phi$  as coordinates of the polarization vec-

tor. The spinor representation (2.2) is thus restricted to the set of orientation states with unit polarization.

With a view to extending the quantum-mechanical representation to states with  $|\mathbf{P}| < 1$ , let us consider the structure of the mean value expression of the  $i$ th component of  $\sigma$ :

$$\begin{aligned} \langle \sigma_i \rangle &= \langle \psi | \sigma_i | \psi \rangle \\ &= \sum_{m,m'=\pm 1/2} \psi_m^* (\sigma_i)_{m'm} \psi_m. \end{aligned} \quad (2.6)$$

This expression can be condensed into the trace of the product of two matrices by combining the spinors  $\psi^*$  and  $\psi$  into a "density matrix"

$$\rho_{mm'} = \psi_m \psi_{m'}^*, \quad (2.7)$$

which yields

$$\langle \sigma_i \rangle = \text{Tr}(\sigma_i \rho) = \sum_{mm'} (\sigma_i)_{m'm} \rho_{mm'}. \quad (2.8)$$

This formula implies that the polarization  $P = |\langle \sigma \rangle|$  reaches unity if, and only if, the matrix  $\rho_{mm'}$  is factorable in accordance with (2.7), that is, if the density operator  $\rho$  is a projection operator with eigenvalues 1 and 0. The operational meaning of these eigenvalues is that a Stern-Gerlach device with its field parallel to  $\mathbf{P}$  deflects the *entire beam* into the + channel, leaving the other component with null intensity. Note that this conceptual procedure for characterizing pure states extends to any quantum system.

### B. Representation of partial polarization<sup>1</sup>

For a state of partial polarization with  $P < 1$ , we may retain Eq. (2.8) to express the mean value of a physical quantity in terms of the matrix  $(\sigma_i)_{m'm}$ —or, more generally,  $A_{m'm}$ —that represents the quantity. The set of elements  $\rho_{mm'}$  of the density matrix in this formula is understood to represent whatever information about the state is necessary and sufficient to predict the mean value of any observable quantity. Conversely, knowledge of a *sufficient set of mean values* determines a set  $\{\rho_{mm'}\}$  and will thus identify the state. Clearly, the matrix  $\rho_{mm'}$  will no longer be factorable, as in Eq. (2.7), for a state of partial polarization, because (2.7) would lead to  $P = 1$ .

General and specific properties of the mean values of a state suffice, in fact, to determine its density matrix by requiring it:

(a) to be Hermitian—otherwise the mean values of some physical quantities would be complex,

(b) to have unit trace—otherwise the mean value of the unit operator would be  $\neq 1$ ,

(c) to have non-negative eigenvalues—otherwise a non-negative operator could have a negative mean value,

(d) to yield  $\langle \sigma \rangle = \mathbf{P}$ .

It will be convenient to represent such a density matrix, as well as any other  $2 \times 2$  Hermitian matrix, as a linear combination of the set of four Hermitian matrices

$$\{1, \sigma_x, \sigma_y, \sigma_z\}. \quad (2.9)$$

This set forms an *orthonormal base*, meaning that the trace of the product of any two *different* set elements vanishes, while the trace of the *square* of each element equals 2. The specifications (a)–(d) of the density matrix imply then that  $\rho$  is represented by

$$\rho = \frac{1}{2}(\mathbb{1} + P_x \sigma_x + P_y \sigma_y + P_z \sigma_z) = \frac{1}{2}(\mathbb{1} + \mathbf{P} \cdot \boldsymbol{\sigma}), \quad (2.10)$$

being thus *identified by the single vector parameter*  $\mathbf{P}$ . Each term of this representation consists of one operator of the set (2.9) multiplied by its mean value; the coefficient  $\frac{1}{2}$  is the reciprocal of the number of mutually orthogonal spin orientations.

An arbitrary Hermitian operator  $A$  with a  $2 \times 2$  matrix is represented by a superposition of the base set (2.9) with coefficients that parametrize the operator,

$$A = a \mathbb{1} + \mathbf{A} \cdot \boldsymbol{\sigma}. \quad (2.11)$$

The mean value of the quantity it represents then takes the form

$$\langle A \rangle = \text{Tr}(A \rho) = a + \mathbf{A} \cdot \mathbf{P}, \quad (2.12)$$

which attains its largest value for states with orientation  $\mathbf{P}$  parallel to  $\mathbf{A}$ . In this notation  $a = \frac{1}{2} \text{Tr} A$  is the mean of the two eigenvalues of  $A$ ,  $|\mathbf{A}|$  is the difference of these eigenvalues, and the vector  $\mathbf{A}$  is parallel to the spin orientation of the eigenvectors of  $A$ . Since  $a$  itself is an invariant aspect of  $A$ , the value of  $\langle A \rangle$  depends essentially on  $|\mathbf{A}|$ ,  $|\mathbf{P}|$ , and  $\hat{A} \cdot \hat{P}$ . We can note particularly the expression

$$\langle \rho \rangle = \text{Tr}(\rho^2) = \frac{1}{2}(1 + |\mathbf{P}|^2), \quad (2.13)$$

a monotonic function of  $|\mathbf{P}|$ , which ranges from  $\frac{1}{2}$  to 1. (Analogous expressions for multiparticle systems will introduce the concept of a generalized polarization.)

Finally, we observe that the general density operator (2.10) has the eigenvalues  $\frac{1}{2}(1 \pm |\mathbf{P}|)$ , which represent the fractional intensities of the two component beams that would be separated by a Stern-Gerlach device with field parallel to  $\mathbf{P}$ . The state is thus often described as the *incoherent* superposition of a base pair of mutually orthogonal pure states with polarization vectors  $\pm \hat{P}$  and weights  $\frac{1}{2}(1 \pm |\mathbf{P}|)$ ; this description is unique except in the extreme case of vanishing polarization, when the direction  $\hat{P}$  remains unspecified.

### C. Time dependence

The action of a magnetic field causes the orientation of a spin to precess about the field direction. To represent this phenomenon we obtain the Schrödinger equation for

<sup>1</sup>Recall that the description of states of partial polarization has presented great difficulties in classical physics, being essentially alien to it. The procedure outlined in this section is instead applicable to all quantum systems.

a density matrix by combining the equations for the spinors  $|\psi\rangle$  and  $\langle\psi|$  of pure states,

$$i\hbar\partial|\psi\rangle/\partial t = H|\psi\rangle, \quad (2.14)$$

$$i\hbar\partial\langle\psi|/\partial t = -\langle\psi|H,$$

to yield

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle\langle\psi| = H|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|H. \quad (2.15)$$

Since any density matrix  $\rho$  can be represented as a linear combination of two matrices for pure states, each obeying (2.15), the equation for  $\rho$  itself reads

$$i\hbar\partial\rho/\partial t = H\rho - \rho H = [H, \rho]. \quad (2.16)$$

In a representation where  $H$  is diagonal, with eigenvalues  $E_m$ , Eq. (2.16) takes the form

$$i\hbar\partial\rho_{mm'}/\partial t = (E_m - E_{m'})\rho_{mm'}, \quad (2.17)$$

with the solution

$$\rho_{mm'}(t) = \rho_{mm'}(0)\exp[-i(E_m - E_{m'})t/\hbar]. \quad (2.18)$$

In the operator notation of Eq. (2.16) the analog of the time dependence (2.18) is

$$\rho(t) = \exp(-iHt/\hbar)\rho(0)\exp(iHt/\hbar). \quad (2.19)$$

Note how only the *observable frequency*,

$$\omega = (E_{1/2} - E_{-1/2})/\hbar, \quad (2.20)$$

occurs in Eqs. (2.17) and (2.18), without any reference to the separate energy eigenvalues  $E_{\pm 1/2}$ , which are themselves defined only to within an arbitrary additive constant. Note also how the formal structure of the expression for the time dependence of an operator's mean value, which combines (2.12) and (2.19),

$$\begin{aligned} \langle A \rangle_t &= \text{Tr}\{A \exp(-iHt/\hbar)\rho \exp(iHt/\hbar)\} \\ &= \sum_{m'm} A_{m'm} \exp(-iE_m t/\hbar) \rho_{m'm} \exp(iE_m t/\hbar), \end{aligned} \quad (2.21)$$

can be read in two alternative but *manifestly equivalent* manners. Grouping the exponentials with  $\rho$  implies that  $\rho$  is time dependent according to Eq. (2.19) (Schrödinger representation), while grouping them with  $A$  implies that  $A$  is time dependent and  $\rho$  constant (Heisenberg representation).

In the familiar example of a particle in a magnetic field  $\mathbf{B}$  we have

$$H = -\frac{1}{2}\gamma\hbar\mathbf{B}\cdot\boldsymbol{\sigma}, \quad (2.22)$$

where  $\gamma$  is the particle's gyromagnetic ratio. In fact, however, any Hamiltonian can be expanded in the form (2.11), which differs from the magnetic example only by the addition of an irrelevant term  $aI$  and by writing  $\mathbf{A}$  in place of  $-\frac{1}{2}\gamma\hbar\mathbf{B}$ . The magnetic example, with  $\mathbf{B}$  parallel to the  $z$  axis, leads to  $\omega = \gamma B$  in Eq. (2.20). Substituting, then,  $H = -\frac{1}{2}\hbar\omega\sigma_z$  in Eq. (2.19), with  $\rho(0)$  in the form

(2.10), and the result in Eq. (2.4), one obtains the precession of  $\mathbf{P}(t)$  represented by

$$\mathbf{P}(t) = \text{Tr}\{e^{i(1/2)\omega t\sigma_z} \frac{1}{2}[\mathbf{1} + \mathbf{P}(0)\cdot\boldsymbol{\sigma}] e^{-i(1/2)\omega t\sigma_z} \boldsymbol{\sigma}\}, \quad (2.23)$$

that is,

$$\begin{aligned} P_x(t) &= \langle\sigma_x\rangle_t = P_x(0)\cos\omega t + P_y(0)\sin\omega t, \\ P_y(t) &= \langle\sigma_y\rangle_t = P_y(0)\cos\omega t - P_x(0)\sin\omega t, \\ P_z(t) &= \langle\sigma_z\rangle_t = P_z(0). \end{aligned} \quad (2.23')$$

A more direct formulation of the precession equation emerges by entering the density matrix expression (2.10) and the Hamiltonian (2.22) in the Schrödinger equation (2.16), working out the commutators of the Pauli matrices. The equation then reduces to the *classical precession equation* for the polarization  $\mathbf{P}$ ,

$$\partial\mathbf{P}/\partial t = -\gamma\mathbf{B}\times\mathbf{P}, \quad (2.24)$$

illustrated by the diagram in Fig. 1. Equation (2.24) may alternatively be introduced at the outset of a treatment of spin precession, as a statement of experimental evidence from which the spinor representation and the Schrödinger equation (2.16) for a pure state are then derived [see Chap. 8 of Fano and Fano (1972)].

#### D. State of thermal equilibrium

According to statistical mechanics, particles with two energy eigenvalues  $E_m$ ,  $m = \pm\frac{1}{2}$ , in equilibrium with a thermostat at temperature  $T$ , are found in either of the corresponding eigenstates  $\psi_m$  with probability

$$\exp(-E_m/kT)/\sum_m \exp(-E_m/kT). \quad (2.25)$$

This amounts to saying that the state of thermal equilibrium is represented by the density operator

$$\rho(T) = \exp(-H/kT)/\text{Tr}[\exp(-H/kT)]. \quad (2.26)$$

When the Hamiltonian has the magnetic form (2.22) with  $\mathbf{B}$  parallel to the  $z$  axis ( $H$  is always equivalent to

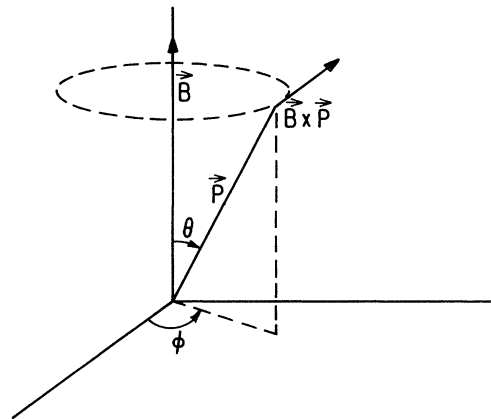


FIG. 1. Diagram of precession equation.

this form, as we know) the density operator depends only on the two operators  $\mathbb{1}$  and  $\sigma_z$  of the set (2.10), since it has axial symmetry about  $z$ . One then finds  $\langle \sigma_z \rangle = \tanh(\gamma B \hbar / 2kT)$ . Accordingly,  $\rho$  is orthogonal to the remaining operators of that set,  $\sigma_x$  and  $\sigma_y$ , meaning that

$$\langle \sigma_x \rangle = \langle \sigma_y \rangle = 0. \tag{2.27}$$

This result is trivially simple but serves as a prototype for a property of all states of thermal equilibrium, namely, that any operator  $O$  orthogonal to all powers of  $H$ , and hence to  $\rho$ —in the sense that  $\text{Tr}(H^n O) = 0$ —has *mean value zero*. A more general phenomenon was anticipated in Sec. I, namely, that all but a few of the parameters required to identify the state of a complex system usually vanish, for reasons analogous to those underlying Eq. (2.22). We shall return to this subject.

### E. Two-level systems

The whole treatment in this section rests on a single point of departure, namely, the existence of an initial pair of orthogonal pure states of spin orientation,  $|\psi_{1/2}\rangle$  and  $|\psi_{-1/2}\rangle$ , whose superpositions—coherent or incoherent—represent all other states. Accordingly, the treatment applies equally to states of any system that are similarly constructed from an initial pair of orthogonal pure states set in one-to-one correspondence to those of spin orientation. Systems from which one abstracts such a base pair of orthogonal states are called “two-level systems.” The relations among their different states and different operators are *isomorphic* to those of spin- $\frac{1}{2}$  orientation, as described, for example, in Chap. 11 of Feynman *et al.* (1965) and in Chap. 9 of Fano and Fano (1972).

We shall concern ourselves particularly with the states of light polarization, for which one usually takes as a base pair either two linear polarizations in orthogonal directions or the pair of right- and left-circular polarizations.

## III. ELECTRON-PROTON SPIN CORRELATIONS

Consider an electron-proton pair, whether bound to form a H atom or unbound in a scattering state. For simplicity we assume orbital motion with  $l=0$  only. An initially uncorrelated spin state of a H atom may be prepared by filtration through a Stern-Gerlach device with a field sufficiently strong to overwhelm the hyperfine interaction. Each beam component selected at the exit of that device then consists of atoms with their electron and proton in specified orientations (up or down) with respect to the field. The spin orientations  $\sigma^e$  and  $\sigma^p$  are uncorrelated in this state, according to definition (1.1), since  $\langle \sigma_x^e \sigma_x^p \rangle = \langle \sigma_x^e \rangle \langle \sigma_x^p \rangle$ . After the exit into free space, the hyperfine interaction controls the orientations of the electron and the proton, forcing them to precess, and thus establishes a correlation between them. I aim here at describing this correlation and the analogous correlation that results from a collision of an electron and a proton

with initially specified orientations.

The orientation of each separate particle is represented, as in Sec. II, by the respective polarization vectors  $\mathbf{P}^e = \langle \sigma^e \rangle$  and  $\mathbf{P}^p = \langle \sigma^p \rangle$ . The correlations of their orientations are then represented through the mean values of products of components of  $\sigma^e$  and  $\sigma^p$ , such as  $\langle \sigma_x^e \sigma_x^p \rangle, \langle \sigma_x^e \sigma_y^p \rangle$ , etc. Analysis of the time dependence of these correlations will then direct our attention to the eigenstates of the hyperfine structure, i.e., to the eigenvectors of the squared total spin  $\frac{1}{4} |\sigma^e \mathbb{1}^p + \mathbb{1}^e \sigma^p|^2 = F(F+1) \mathbb{1}^e \mathbb{1}^p$  and of one of its components,  $\frac{1}{2} (\sigma_z^e \mathbb{1}^p + \mathbb{1}^e \sigma_z^p)$ , which are linear combinations of operator products. Consideration of relevant symmetries will help us in mapping out the manifold relevant relationships.

When two particles separate after a collision—or after dissociation of a bound state—often only one of the two remains under observation. Predictions on the results of such observations utilize only a part of the data on the state of the whole pair, leaving out, in particular, any information on the correlations of the two particles. This process of data elimination will be seen to lie at the root of irreversibility.

The vector and tensor operator approach to be utilized here dates from the 1950s. This approach has been applied extensively to the particular, if important, classes of correlations generated by spin-spin, spin-orbit, and spin-external-field scalar coupling in atomic systems. Effects of these correlations have been prominent in the study of nuclear spectroscopy (Siegbahn, 1965), of optical pumping (Happer, 1972; Omont, 1977), and of the inferences drawn from optical emission (Fano and Macek, 1973). This section will face the broader task of considering the whole class of correlations that may occur between the orientations of two particles with spin  $\frac{1}{2}$ .

### A. Base set of operator products

As the density matrix of a single spin is represented by a superposition of the set of four Pauli operators in Eq. (2.10), so can we represent the matrix  $\rho^{ep}$  for the combination of electron and proton spin as a superposition of the set of 16 direct products of electron and proton operators

$$\{ \mathbb{1}^e \mathbb{1}^p, \mathbb{1}^e \sigma_x^p, \mathbb{1}^e \sigma_y^p, \mathbb{1}^e \sigma_z^p, \sigma_x^e \mathbb{1}^p, \dots, \sigma_x^e \sigma_x^p, \sigma_x^e \sigma_y^p, \dots, \sigma_z^e \sigma_x^p \}, \tag{3.1}$$

which may be indicated by the array

$$\begin{Bmatrix} \mathbb{1}^e \mathbb{1}^p & \mathbb{1}^e \sigma^p \\ \sigma^e \mathbb{1}^p & \sigma^e \sigma^p \end{Bmatrix}. \tag{3.1'}$$

The set of 16 operators (3.1) is orthonormal and complete in the same sense as the set (2.9) is for a single spin;

- (a) the trace of the square of each operator equals 4;
- (b) the trace of the product of any two different elements vanishes;
- (c) any operator acting on the orientations of the spin

pair can be represented as a linear superposition of the set (3.1).

The mean value of a product of operators acting on the electron and proton, respectively, is then represented by the analog of Eq. (2.8),

$$\langle A^e B^p \rangle = \text{Tr}(A^e B^p \rho^{ep}) . \tag{3.2}$$

Lack of correlation between the two spin orientations is defined, according to (1.1), as

$$\langle A^e B^p \rangle_{\text{uncorr}} = \langle A^e \mathbb{1}^p \rangle \langle \mathbb{1}^e B^p \rangle , \tag{3.3}$$

from which follows

$$\rho_{\text{uncorr}}^{ep} \equiv \frac{1}{2} (\mathbb{1}^e + \mathbf{P}^e \cdot \boldsymbol{\sigma}^e) \frac{1}{2} (\mathbb{1}^p + \mathbf{P}^p \cdot \boldsymbol{\sigma}^p) . \tag{3.4}$$

In the example of H atoms filtered through a strong-field Stern-Gerlach device, i.e., under Paschen-Back conditions, the component with electron spin-up and proton spin-down is characterized by  $\mathbf{P}^e = \hat{z}$  and  $\mathbf{P}^p = -\hat{z}$ , that is, by

$$\rho_{\text{uncorr}}^{ep} = \frac{1}{4} (\mathbb{1}^e + \sigma_z^e) (\mathbb{1}^p - \sigma_z^p) . \tag{3.4'}$$

For a general state, with correlated orientations, the same considerations that led us to Eq. (2.10) lead now to the density matrix representation

$$\rho^{ep} = \frac{1}{4} [(\mathbb{1}^e + \mathbf{P}^e \cdot \boldsymbol{\sigma}^e)(\mathbb{1}^p + \mathbf{P}^p \cdot \boldsymbol{\sigma}^p) + \boldsymbol{\sigma}^e \cdot \mathcal{C}^{ep} \cdot \boldsymbol{\sigma}^p] , \tag{3.5}$$

where the parameter  $\mathcal{C}^{ep}$  indicates a tensor whose components

$$\begin{pmatrix} C_{xx}^{ep} & C_{xy}^{ep} & C_{xz}^{ep} \\ C_{yx}^{ep} & C_{yy}^{ep} & C_{yz}^{ep} \\ C_{zx}^{ep} & C_{zy}^{ep} & C_{zz}^{ep} \end{pmatrix}$$

represent the correlations,  $C_{xx}^{ep} = \langle \sigma_x^e \sigma_x^p \rangle - \langle \sigma_x^e \rangle \langle \sigma_x^p \rangle$ ,  $C_{xy}^{ep} = \langle \sigma_x^e \sigma_y^p \rangle - \langle \sigma_x^e \rangle \langle \sigma_y^p \rangle$ , etc. The parameters of the matrix (3.5) may be blocked out as an array analogous to (3.1'),

$$\left\{ \begin{matrix} 1 & \mathbf{P}^p \\ \mathbf{P}^e & \mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep} \end{matrix} \right\} . \tag{3.6}$$

The structure of the density matrix (3.5) parallels that of the single-particle equation (2.10): Each term in the curly brackets is the product of one operator of the set (3.1') and of its mean value, which is represented by one parameter of the set (3.6); the coefficient  $\frac{1}{4}$  is the reciprocal of the dimension of the matrices  $\sigma_i^e \sigma_j^p$ , i.e., of the number of mutually orthogonal states of the particle pair.

The value of the parameters  $\mathbf{P}^e$ ,  $\mathbf{P}^p$ , and  $\mathcal{C}^{ep}$  are restricted by the physical considerations of Sec. II.B. In particular, we have

$$\begin{aligned} \langle \rho^{ep} \rangle &= \text{Tr}[(\rho^{ep})^2] = \frac{1}{4} \{ 1 + |\mathbf{P}^e|^2 + |\mathbf{P}^p|^2 + \text{Tr}[(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^2] \} \\ &= \frac{1}{4} \{ (1 + |\mathbf{P}^e|^2)(1 + |\mathbf{P}^p|^2) + 2 \sum_{ik} P_i^e C_{ik} P_k^p + \sum_{ik} C_{ik}^2 \} \leq 1 , \end{aligned} \tag{3.7}$$

or, equivalently,

$$|\mathbf{P}^e|^2 + |\mathbf{P}^p|^2 + |\mathbf{P}^e|^2 |\mathbf{P}^p|^2 + 2 \mathbf{P}^e \cdot \mathcal{C}^{ep} \cdot \mathbf{P}^p + |\mathcal{C}^{ep}|^2 \leq 3 . \tag{3.7'}$$

The expression on the left of (3.7') may be viewed as the squared magnitude of a generalized polarization vector whose 15 components are the 15 nontrivial parameters of the array (3.6). The ceiling value 3 on the right derives from the number of mutually orthogonal states of two spins, namely, 4, which appears in the denominator of (3.7), reduced by unity to eliminate the trivial contribution of the unit operator  $\mathbb{1}^e \mathbb{1}^p$  to  $\rho^2$ . The inequality (3.7), or (3.7'), requires, for example,  $\mathcal{C}^{ep}$  to vanish when  $|\mathbf{P}^e| = |\mathbf{P}^p| = 1$ , much as  $P_x$  and  $P_y$  vanish in (2.10) when  $P_z = 1$ .

As the vector  $\mathbf{P}$  represents the state of orientation of a single spin in Sec. II, so does the 15-component aggregate  $\{\mathbf{P}^e, \mathbf{P}^p, \mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}\}$  represent the joint state of a pair of spins. This aggregate may in fact be viewed as the set of components of a vector  $\rho^{ep}$  in a 15-dimensional model space spanned by the operators  $\{\sigma^e \mathbb{1}^p, \mathbb{1}^e \sigma^p, \sigma^e \sigma^p\}$  serving as unit vectors. This representation of the state of a quantum system, to be utilized throughout this article, is called the Liouville representation in statistical mechan-

ics, with reference to its classical analog with phase-space coordinates  $\{q_i, p_i\}$ .

Two distinct types of transformation of the representation (3.5) of  $\rho^{ep}$ , viewed as a vector, will be utilized in the following:

(a) Simultaneous reciprocal unitary transformations of both sets  $\{\mathbf{P}^e, \mathbf{P}^p, \mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}\}$  and  $\{\sigma^e \mathbb{1}^p, \mathbb{1}^e \sigma^p, \sigma^e \sigma^p\}$ , which leave  $\rho^{ep}$  invariant and amount only to a change of coordinate frame in the Liouville space. These transformations will be utilized in Sec. III.B.

(b) Actual transformations of  $\rho^{ep}$  which take place in the course of time or as a result of a collision or other action. These consist of a unitary transformation of the set  $\{\mathbf{P}^e, \mathbf{P}^p, \mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}\}$  alone in the Schrödinger representation, or alternatively of the reciprocal transformation of  $\{\sigma^e \mathbb{1}^p, \mathbb{1}^e \sigma^p, \sigma^e \sigma^p\}$  in the Heisenberg representation. This second type amounts to a precession of  $\rho^{ep}$  analogous to the precession of  $\mathbf{P}$  according to Eq. (2.24) and will be introduced in Sec. III.C. Thus one views the density operator as precessing in Liouville space just as a state vector  $\psi$  precesses in the usual Hilbert space. The diagram of Fig. 1 might serve to visualize this precession in a model space, even though the Liouville model space coincides with physical space only in the simple case of a single spin.

Unitary transformations in the Liouville model space have been used for a long time, being described, for instance, in Secs. 6 and 7 of Fano (1957), where their infinitesimal elements are indicated by  $\Omega_{ik}$ . These operations have been called by different names in different contexts; the term "superoperators" is familiar, for example, in the literature of magnetic resonance. Their conceptual role underlies much of the present article without requiring any explicit formulation.

## B. Symmetrized operators and state parameters

The complete set of 15 nontrivial operators (3.1) is so numerous—even in this example with only two particles—that one wants to structure it into subsets. The blocking in Eq. (3.1') already sorts out two vectors and the dyadic tensor  $\sigma^e \sigma^p$ . Analysis by rotation and reflection symmetries is appropriate, say, in hyperfine structure experiments with magnetic field  $B\hat{z}$ , in which case the operator  $\gamma_e \sigma_z^e \mathbf{1}^p + \mathbf{1}^e \gamma_p \sigma_z^p$ , involving the particle gyromagnetic ratios, is a constant of the motion. In scattering experiments with initial and final momenta  $\mathbf{p}_i$  and  $\mathbf{p}_f$  (in the center of mass system), the  $z$  axis is usually laid along the vector  $\mathbf{p}_i \times \mathbf{p}_f$  and the spin angular momentum in this direction is particularly relevant.

Much of the success of mapping two-level systems onto a spin orientation derives from the intuitive ease of following the motion of the vector  $\mathbf{P}$ , which represents the spin's orientation. Symmetry analysis of the parameters (3.6) aims at the same goal of developing a convenient geometrical mapping for the parameters of multiparticle and/or multilevel systems. Familiarity with tensorial parameters and with their symmetries is not achieved as easily as for vectors, but it serves the same purposes. Progress toward this familiarity has proven very rewarding over the years, to this author at least. Effective utilization of symmetries for the classification and manipulation of multiparticle state parameters is an open-ended endeavor, toward which I present here introductory material.

The nine-component dyadic tensor  $\sigma^e \sigma^p$  can be sorted out further into irreducible parts that transform like spherical harmonics under coordinate rotations. Thus one singles out

(a) the scalar

$$\sigma^e \cdot \sigma^p, \quad (3.8a)$$

which measures how parallel the two spin orientations are and whose eigenvalues,  $-3$  and  $1$ , correspond to the total angular quantum numbers  $F=0$  and  $1$ , respectively,

(b) the vector

$$\sigma^e \times \sigma^p, \quad (3.8b)$$

which measures the amount of transverseness to one another of the two spins  $\sigma^e$  and  $\sigma^p$ ,<sup>2</sup> and

<sup>2</sup>However, the mean values  $\langle \sigma^e \times \sigma^p \rangle$ ,  $\langle \sigma^e \rangle$ , and  $\langle \sigma^p \rangle$  may be collinear, even though  $\langle \sigma^e \rangle \times \langle \sigma^p \rangle$ ,  $\langle \sigma^e \rangle$ , and  $\langle \sigma^p \rangle$  may not.

(c) the five components

$$\begin{aligned} U_0^{(2)} &= \sqrt{1/6}(3\sigma_z^e \sigma_z^p - \sigma^e \cdot \sigma^p), \\ U_{\pm 1}^{(2)} &= \mp \frac{1}{2}[(\sigma_x^e \sigma_z^p + \sigma_z^e \sigma_x^p) \pm i(\sigma_y^e \sigma_z^p + \sigma_z^e \sigma_y^p)] \\ &= \mp \sqrt{1/2}(\sigma_{\mp}^e \sigma_z^p + \sigma_z^e \sigma_{\pm}^p), \\ U_{\pm 2}^{(2)} &= \frac{1}{2}[(\sigma_x^e \sigma_x^p - \sigma_y^e \sigma_y^p) \pm i(\sigma_x^e \sigma_y^p + \sigma_y^e \sigma_x^p)] \\ &= \sigma_{\pm}^e \sigma_{\pm}^p, \end{aligned} \quad (3.8c)$$

whose mean values identify the quadrupole moment of the two-particle system. Tensor components with these symmetries represent the interaction of dipole and quadrupole moments of a system with appropriate field configurations.<sup>3</sup>

Besides the operator symmetry under coordinate rotations we consider their symmetry under the electron-proton permutation operator  $\mathcal{P}^{ep}$ . The operators (3.8) are already eigenvectors of this operator, the scalar and quadrupole being even and the vector odd. The vectors  $\sigma^e \mathbf{1}^p$  and  $\mathbf{1}^e \sigma^p$  of the set (3.1') are instead asymmetric; symmetrization replaces them by the pair of eigenvectors of  $\mathcal{P}^{ep}$ ,

$$\sqrt{1/2}(\sigma^e \mathbf{1}^p + \mathbf{1}^e \sigma^p), \quad (3.9a)$$

$$\sqrt{1/2}(\sigma^e \mathbf{1}^p - \mathbf{1}^e \sigma^p), \quad (3.9b)$$

the first of which represents the total spin angular momentum of the particles.

The entire expansion (3.5) of the density matrix  $\rho^{ep}$  in terms of operator products can be transformed into an expansion in the 15 symmetrized operators (3.8) and (3.9), whose coefficients are combinations of the 15 parameters  $\mathbf{P}^e, \mathbf{P}^p$ , and  $\mathcal{C}^{ep}$  contragredient to the operator combinations. A prototype transformation of this type is described on pp. 14 and 15 of Fano and Racah (1959).

The symmetry of the operators under  $\mathcal{P}^{ep}$  serves to classify their action on stationary states of the  $e-p$  system in zero field, because these states are themselves eigenstates of  $\mathcal{P}^{ep}$ , odd for  $F=0$  and even for  $F=1$ . It follows that the nine even parity operators, (3.8a), (3.8c), and (3.9a), are *diagonal in F*, while the six odd operators, components of the vectors (3.8b) and (3.9b), are *off diagonal*. This result will prove essential as we move on to discuss the time dependence of the two-particle state.

A further consideration completes the symmetry analysis of our 15 operators. Whenever the symmetry group of the states of a system has a subgroup of two operators,  $\{1, \mathcal{P}^{ep}\}$  in our case, half of the matrices of

<sup>3</sup>Each pure state of a particle or other localized system can be identified as its state of lowest energy when subjected to a specified field configuration. In the example of the degenerate manifold of  $p$  states of an electron in a central field, the energy of any one pure state reaches its lowest eigenvalue when the system is placed in the center of the disposition of a coil and condenser, as shown in Fig. 2. The three Euler angles identifying the orientation of this disposition combine with the ratio (coil current)/(condenser charge) to yield the four parameters that identify the particular state within its manifold.

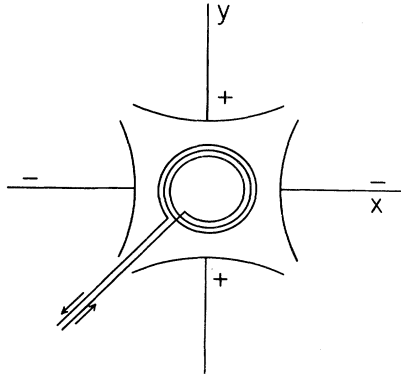


FIG. 2. Magnetizing coil and quadrupole condenser providing a field configuration with Hamiltonian  $aJ_z + b(U_2^+ + U_2^-)$  [from Fano (1968)].

Hermitian parity-changing operators are symmetric and half antisymmetric. Non-Hermitian raising and lowering operators can then be constructed which change the parity only from odd to even or even to odd, respectively. In our case the  $F$ -raising and  $F$ -lowering operators are

$$\mathbf{M}^\pm = \frac{1}{2}[(\sigma^e \mathbb{1}^p - \mathbb{1}^e \sigma^p) \pm i\sqrt{2}(\sigma^e \times \sigma^p)]$$

$$\rightarrow \begin{cases} F=0 \rightarrow F=1 \\ F=1 \rightarrow F=0 \end{cases} \quad (3.10)$$

as one can verify by constructing their matrices. Operators that raise or lower the magnetic quantum number are similarly constructed by the usual combination of  $x$  and  $y$  components of the vector operators.<sup>4</sup> Application of the same approach to symmetry under coordinate reflection through the  $(x,y)$  plane follows in a later section.

The symmetry analysis of the operator set (3.1') remains to be complemented by a corresponding analysis of the parameter set (3.6). Specifically, the expressions

$$\rho^{ep} = \frac{1}{4} \{ \mathbb{1}^e \mathbb{1}^p + \frac{1}{2}(\mathbf{P}^e + \mathbf{P}^p) \cdot (\sigma^e \mathbb{1}^p + \mathbb{1}^e \sigma^p) + \frac{1}{3}(\mathbf{P}^e \cdot \mathbf{P}^p + \mathcal{C}^{ep})^{(0)} \sigma^e \cdot \sigma^p + (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(2)*} \cdot \mathbf{U}^{(2)} + \frac{1}{2}[(\mathbf{P}^e - \mathbf{P}^p) - i\sqrt{2}(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)}] \cdot \mathbf{M}^+ + \frac{1}{2}[(\mathbf{P}^e - \mathbf{P}^p) + i\sqrt{2}(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)}] \cdot \mathbf{M}^- \} \quad (3.13)$$

The asterisk in (3.13) indicates complex conjugation and  $\cdot$  indicates a scalar product, that is, summing over component products with equal indices.

### C. Time dependence and scattering

A pair of spins that are neither parallel nor antiparallel precesses about their total angular momentum in classical

<sup>4</sup>In the two-level example of {spin-up, spin-down} states the subgroup of operations  $\{1, \sigma_z\}$  is an analog of  $\{1, \mathcal{P}^{ep}\}$ , since spin-up (-down) is even (odd) with respect to  $\sigma_z$ . The two operators  $\{\sigma_x, \sigma_y\}$  interchange spin up with spin down, thereby interchanging their parities with respect to  $\sigma_z$ ; of these,  $\sigma_x$  is symmetric,  $\sigma_y$  antisymmetric. Their combinations  $\sigma_x \pm i\sigma_y$  are prototype spin-raising (-lowering) operators, which change the parity with respect to  $\sigma_z$  from odd to even, or from even to odd, respectively.

(3.8) are complemented by corresponding expressions derived from the tensor parameters  $\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}$  of (3.6). These expressions consist of

(a) the scalar

$$(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(0)} = \mathbf{P}^e \cdot \mathbf{P}^p + C_{xx}^{ep} + C_{yy}^{ep} + C_{zz}^{ep}, \quad (3.11a)$$

(b) a vector consisting of  $\mathbf{P}^e \times \mathbf{P}^p$  and of a corresponding part of  $\mathcal{C}^{ep}$  with components

$$(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)}_x = P_y^e P_z^p - P_z^e P_y^p + C_{yz}^{ep} - C_{zy}^{ep}, \quad (3.11b)$$

etc., and

(c) a five-component tensor with components analogous to (3.8c)

$$(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(2)}_0 = \sqrt{1/6}(3P_z^e P_z^p - \mathbf{P}^e \cdot \mathbf{P}^p + 2C_{zz}^{ep} - C_{xx}^{ep} - C_{yy}^{ep}), \quad (3.11c)$$

etc.

The expressions (3.11a) and (3.11c) are even under the permutation  $\mathcal{P}^{ep}$ , while (3.11b) is odd. The odd vector (3.11b) then combines with the analog of (3.9b),  $\sqrt{1/2}(\mathbf{P}^e - \mathbf{P}^p)$ , to yield the parameters contragredient to (3.10), namely,

$$\frac{1}{2}[(\mathbf{P}^e - \mathbf{P}^p) \mp i\sqrt{2}(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)}]. \quad (3.12)$$

Figure 3 shows a diagram of  $\mathbf{P}^e$ ,  $\mathbf{P}^p$ ,  $\frac{1}{2}(\mathbf{P}^e \mp \mathbf{P}^p)$ , and  $\mathbf{P}^e \times \mathbf{P}^p$  vectors. The antisymmetric part of  $\mathcal{C}^{ep}$  is similarly represented by a vector; its symmetric components would be jointly represented by an ellipsoid in the same space.

The entire density matrix (3.5) now takes the form of a sum of products of symmetrized parameters and symmetrized matrices

or quantum mechanics and in the absence of an external field. We shall see now how this precession emerges in our formalism. However, it will emerge only indirectly through spin correlations in our example of a quantum state whose mean angular momentum vanishes while its mean square does not. The symmetry analysis of Sec. III.B will prove very helpful.

The time-dependent Eq. (2.16) for a density matrix holds for all systems, as is apparent from its derivation, and so does its formal solution, Eq. (2.19). This solution simplifies for our example, much as it did for the single-particle Hamiltonian (2.22), because the electron-proton spin Hamiltonian,

$$H^{ep} = b \sigma^e \cdot \sigma^p, \quad (3.14)$$

is a scalar symmetric under  $\mathcal{P}^{ep}$ .  $H^{ep}$  yields only two levels of opposite parity, whereby it commutes with all even



parity terms of  $\rho^{ep}$ . Only the odd terms of  $\rho^{ep}$ , proportional to  $\frac{1}{2}(\sigma^e \mathbf{1}^p - \mathbf{1}^e \sigma^p)$  and to  $\sigma^e \times \sigma^p$ , oscillate with the single frequency of the spectrum of  $H^{ep}$ ,

$$\omega = (E_{F=1} - E_{F=0}) / \hbar = 4b / \hbar. \quad (3.15)$$

Construction of an explicit representation of these oscillations, analogous to Eq. (2.23) for a single spin, requires us to sort out the terms of  $\rho^{ep}$  proportional to  $\cos \omega t$  and  $\sin \omega t$ , respectively. To this end, one notices first that in the time-dependent expansion of  $\rho^{ep}(t)$ , Eq. (2.19), all the terms of  $\rho^{ep}$  diagonal in  $F$  commute with  $H^{ep}$  and remain constant. The  $F$ -raising and  $F$ -lowering terms, on the other hand, have an exponential time dependence, since

$$\exp(-iH^{ep}t/\hbar) \mathbf{M}^\pm \exp(iH^{ep}t/\hbar) = \mathbf{M}^\pm \exp(\mp i\omega t). \quad (3.10')$$

Accordingly, the density matrix expression (3.13) is made time dependent simply by adding factors  $e^{-i\omega t}$  and  $e^{i\omega t}$ , respectively, to its last two lines. Separating the  $\cos \omega t$  and  $\sin \omega t$  terms of these exponentials, we obtain

$$\begin{aligned} \rho^{ep}(t) = & \frac{1}{4} \{ \mathbf{1}^e \mathbf{1}^p + \frac{1}{2} (\mathbf{P}^e + \mathbf{P}^p) \cdot (\sigma^e \mathbf{1}^p + \mathbf{1}^e \sigma^p) + \frac{1}{3} (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(0)} \sigma^e \cdot \sigma^p + (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(2)*} \cdot \mathbf{U}^{(2)} \\ & + \frac{1}{2} [(\mathbf{P}^e - \mathbf{P}^p) \cos \omega t - (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)} \sin \omega t] \cdot (\sigma^e \mathbf{1}^p - \sigma^p \mathbf{1}^e) \\ & + \frac{1}{2} [(\mathbf{P}^e - \mathbf{P}^p) \sin \omega t + (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)} \cos \omega t] \cdot \sigma^e \times \sigma^p \}. \end{aligned} \quad (3.16)$$

The parameters  $\mathbf{P}^e$ ,  $\mathbf{P}^p$ , and  $\mathcal{C}^{ep}$  in Eq. (3.16) are understood to be time independent. In a Schrödinger representation, on the other hand, one regards the coefficient of  $\sigma^e \mathbf{1}^p - \mathbf{1}^e \sigma^p$  in Eq. (3.16) as representing  $\frac{1}{2}(\mathbf{P}^e - \mathbf{P}^p)$  at the time  $t$ . Indicating this time dependence by an index  $t$ , we obtain from Eq. (3.16) the representation of time dependence

$$(\mathbf{P}^e - \mathbf{P}^p)_t = (\mathbf{P}^e - \mathbf{P}^p)_0 \cos \omega t - (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_0^{(1)} \sin \omega t, \quad (3.17a)$$

$$(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_t^{(1)} = (\mathbf{P}^e - \mathbf{P}^p)_0 \sin \omega t + (\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_0^{(1)} \cos \omega t. \quad (3.17b)$$

Considering that the  $(\mathbf{P}^e \times \mathbf{P}^p)_0$  portion of  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_0^{(1)}$  is orthogonal to both  $(\mathbf{P}^e \pm \mathbf{P}^p)_0$ , we can see that Eq. (3.17a) represents the precession of  $(\mathbf{P}^e - \mathbf{P}^p)_t$  about the constant angular momentum  $\frac{1}{2}(\mathbf{P}^e + \mathbf{P}^p)_0$ , which is described in an elementary treatment of hyperfine coupling (Fig. 3). The time-dependent polarization vectors  $\mathbf{P}_t^e$  and  $\mathbf{P}_t^p$  are thus completely determined by Eq. (3.17a) and by the constant vector  $(\mathbf{P}^e + \mathbf{P}^p)_0$ .

The time dependence of the correlation tensor  $(\mathcal{C}^{ep})_t$  is obtained in a second step, utilizing

(a) the constant parameters  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(0)}$  and  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(2)}$ ,

(b) the time-dependent parameter  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_t^{(1)}$  given by Eq. (3.17b), and

(c) the previously determined  $\mathbf{P}_t^e$  and  $\mathbf{P}_t^p$ . This pro-

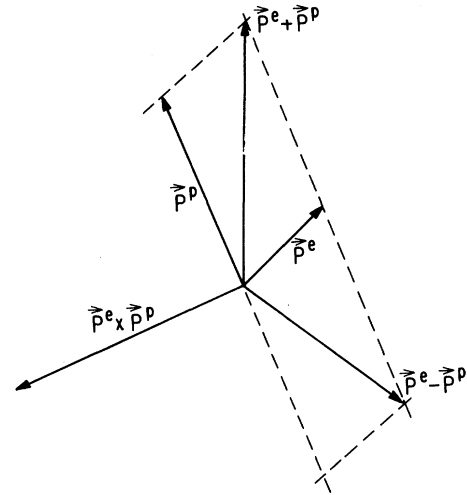


FIG. 3. Polarization vectors for a pair of spins and their combinations. The whole set of vectors will precess about  $\mathbf{P}^e + \mathbf{P}^p$  under the influence of  $\sigma^e \cdot \sigma^p$  interaction.

cedure reflects the fact that the correlation tensor  $\mathcal{C}^{ep}$  is defined, according to (1.1), as the difference of the separately measurable tensors  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})_t$  and  $\mathbf{P}_t^e \mathbf{P}_t^p$ .

As an illustration we obtain here the explicit values of the nonzero components of  $\mathbf{P}_t^e \mathbf{P}_t^p$  and  $\mathcal{C}_t^{ep}$  for our example of H atoms. The atoms are prefiltered through a Stern-Gerlach device with a very strong field, such that they exit in free space at  $t=0$  with their electron and proton spins fully polarized in opposite directions,<sup>5</sup>

$$\mathbf{P}_0^e = \hat{z}, \quad \mathbf{P}_0^p = -\hat{z}, \quad \mathcal{C}_0^{ep} = 0. \quad (3.18)$$

Their state is accordingly represented by the uncorrelated matrix (3.4')

$$\rho_0^{ep} = \rho_{\text{uncorr}}^{ep} = \frac{1}{4} (\mathbf{1}^e \mathbf{1}^p + \sigma_z^e \mathbf{1}^p - \mathbf{1}^e \sigma_z^p - \sigma_z^e \sigma_z^p). \quad (3.19)$$

Entering the parameters (3.18) in Eqs. (3.17), and remarking that  $\mathbf{P}_0^e \times \mathbf{P}_0^p = 0$ , gives

$$\begin{aligned} (\mathbf{P}^e - \mathbf{P}^p)_t &= 2\hat{z} \cos \omega t, \\ (\mathcal{C}^{ep})_t^{(1)} &= 2\hat{z} \sin \omega t \end{aligned} \quad (3.20)$$

<sup>5</sup>This specification of the initial state implies "sudden" exit from the Stern-Gerlach magnet, in contrast to the usual quasiadiabatic exit through a fringing field. A sudden variation of a magnetic field along a beam is assumed here for purposes of schematization but has actually been achieved by special devices (Frisch and Segrè, 1933).

or equivalently, since  $\mathbf{P}^e + \mathbf{P}^p = 0$ ,

$$\begin{aligned} P_{zt}^e &= \cos\omega t, & P_{zt}^p &= -\cos\omega t, \\ C_{xy}^{ep} &= -C_{yz}^{ep} = \sin\omega t. \end{aligned} \quad (3.21)$$

The last of these results shows that  $\langle \sigma_x^e \sigma_y^p - \sigma_y^e \sigma_x^p \rangle_t$  does not vanish, even though  $\langle \sigma_x^e \rangle$ ,  $\langle \sigma_y^e \rangle$ ,  $\langle \sigma_x^p \rangle$ , and  $\langle \sigma_y^p \rangle$  do.

One further component of  $\mathcal{C}_t^{ep}$  is nonzero. Substitution of the initial data (3.18) into the constant parameters (3.11a) and (3.11c) shows them to be equal to  $-1$  and  $-2\sqrt{1/6}$ , respectively, in accordance with the value  $-1$  of the coefficient of  $\sigma_x^e \sigma_z^p$  in (3.19). However, the product  $(P_z^e P_z^p)_t$  does not remain equal to  $-1$  in the course of time but equals  $-\cos^2\omega t$ . Constancy of (3.11a) and (3.11c) then requires that

$$C_{zz}^{ep} = -\sin^2\omega t. \quad (3.22)$$

In this example the initial-state parameters (3.18) have axial symmetry about the  $\hat{z}$  axis. This symmetry is preserved in the course of time, as seen in (3.20) and (3.22), because the Hamiltonian (3.14) is scalar and hence also axisymmetric. The “precession” induced by the spin coupling degenerates in this case into axial oscillations of the parameters. An ordinary precession would instead be induced by the same Hamiltonian, according to (3.17), if the state vectors  $\mathbf{P}^e - \mathbf{P}^p$  and/or  $(\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep})^{(1)}$  had nonzero  $x$  or  $y$  components at the initial time  $t = 0$ .

Finally, we complement the discussion of the time-dependent  $\rho^{ep}(t)$  by showing how it adapts readily to the matrix  $\rho_f^{ep}$  that represents the final state of spin orientation of an electron and proton following their collision. Prior to the collision, the density matrix  $\rho_i^{ep}$  represents a state of independent orientations of the pair and has accordingly the uncorrelated form (3.4). The collision effect is represented by a scattering matrix  $S$ , which plays here the same role as the general time evolution operator  $\exp(-iHt/\hbar)$  does in Eq. (2.19), yielding

$$\rho_f^{ep} = S \rho_i^{ep} S^{-1}. \quad (3.23)$$

The scattering matrix has the general familiar form  $\langle \mathbf{p}_f m_f | S | \mathbf{p}_i m_i \rangle$ , where  $\mathbf{p}$  indicates the collision momentum and  $m$  the magnetic quantum numbers of electron and proton. Considering initially only the  $l=0$  partial wave, we notice that the dependence of  $S$  on the orientation quantum numbers becomes diagonal in the representation of stationary states  $(F, M)$ , where it reduces to

$$\langle F' M' | S | F M \rangle = \exp(2i\delta_F) \delta_{FF'} \delta_{MM'}. \quad (3.24)$$

The expression of  $\rho_f^{ep}$  is thus obtained from that of  $\rho^{ep}(t)$  by simply replacing  $\omega t$  with the double phase-shift difference  $2(\delta_1 - \delta_0)$ . The Coulomb interaction adds to (3.23) a further factor  $\exp(2i\delta_{C0})$ , where  $\delta_{C0}$  is the ordinary Coulomb phase shift for the  $l=0$  channel at the relevant energy. For  $l \neq 0$  the Coulomb phase shift has different values  $\delta_{Cl}$ , but the spin factor (3.24) reduces approximately to unity, because the electron and proton do not come into contact.

#### D. Conservation law

In the earlier discussion of a single spin we saw how the polarization vector  $\mathbf{P}$  merely rotates in the course of time according to Eq. (2.24), keeping its magnitude constant. Similarly, the oscillations of the two-particle set of parameters listed in Eq. (3.6) amount to an orthogonal transformation which leaves the *sum of their squares invariant* on the left of Eq. (3.7'). Indeed, according to Sec. III.A, one may regard the parameters of the set (3.6)—excluding unity—as the components of a 15-dimensional vector  $\mathbf{V}$  which represents a generalized polarization of the particle pair and merely rotates in the course of time or as a result of collisions. This fundamental conservation law is implicit in the solution (2.19) of the Schrödinger equation, that is, in the Hamiltonian character of quantum mechanics. The density matrix merely experiences an equivalence transformation which leaves invariant its eigenvalues and hence the  $\text{Tr}(\rho^n)$  for all values of  $n$ . In particular, the left-hand side (lhs) of Eq. (3.7) remains invariant.

The sum of squared parameters on the left of (3.7') thus serves as an index of the *overall polarization* of the particle pair, that is, of the departure of its state from the amorphous condition in which all nonunity parameters of the set (3.6) vanish and with them the lhs of Eq. (3.7'). This sum has also been called the “quantity of information” about the pair, but the concept and noun “information” have been used in inequivalent manners. Recall here that the density matrix (3.5) provides, in fact, a *fully specified* description of the state of the system by predicting the mean values of any operator. Let it be stressed that the vanishing of any, or all, of the coefficients of operators in the expansion (3.5) or (3.13) of  $\rho^{ep}$  constitutes a *definite prediction* concerning experimental measurements and should *not* be construed as a statement of ignorance about a significant variable. The concept of “information” is accordingly inappropriate here.

The representation of the state of a spin pair by a vector  $\mathbf{V}$  in the 15-dimensional model space of parameters  $\mathbf{P}^e, \mathbf{P}^p, \mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}$  provides a model for further developments. The parameter oscillations described by Eqs. (3.21)–(3.22), or their analogs, are viewed in this picture as variations of the projection of  $\mathbf{V}$  onto particular coordinate axes, reflecting the vector's rotation in the course of time. Recalling how the sum of squared parameters on the left of Eq. (3.7') represents the squared magnitude  $|\mathbf{V}|^2$ , we see the state's evolution as merely redistributing their constant sum among its various terms. Such a redistribution becomes, however, very significant when it effectively subtracts from components under observation, transferring polarization to components that are practically inaccessible to observation; polarization would be effectively dissipated in this event.

#### E. Reversibility and its practical limits

The evolution of a quantum system governed by the time-dependent Schrödinger equation is, in principle, ex-

actly reversible in time, just as its classical Hamiltonian analog is. By this is meant that sudden sign reversal of all velocities of a system at a time  $t > 0$  will bring the state at time  $2t$  back to where it was at  $t = 0$ . The phenomena of spin echo (Hahn, 1950) and photon echo (Kurnit *et al.*, 1964) demonstrate this reversibility, to within imperfections of the sudden reversal of the precession of a spin assembly.

A more relevant question concerns the extent to which the predictive power embodied in the initial knowledge of the polarization vector  $\mathbf{V}$  can be retrieved at later times or is instead dissipated irretrievably. This question is touched upon here first with reference to our two-spin prototype and then to anticipated behavior of more complex systems. We shall return to this question in Sec. V.D.

Let us first consider the example of an electron-proton collision outlined at the end of Sec. III.C. The initial state of the spin pair is "pure," with  $|\mathbf{P}^e| = |\mathbf{P}^p| = 1$ , which makes the left-hand side of the squared polarization, Eq. (3.7'), equal to 3. The collision transformation, (3.23), will generally transfer part of the polarization to components of the correlation tensor  $\mathcal{C}^{ep}$ . These components of the state of the electron-proton pair remain indeed observable through coincidence experiments on the two particles after collision, but will no longer contribute to further evolution of the spin pair. In particular,  $\mathcal{C}^{ep}$  will no longer return to its initial value zero, thus preventing  $|\mathbf{P}^e|$  and  $|\mathbf{P}^p|$  from ever returning to unity. This argument applies to any interaction of finite duration.

Within the scope of a bound state of the spin pair, which evolves steadily in time, the evolution of the polarization vector  $\mathbf{V}$  described in Sec. III.C follows a singly periodic track which brings  $|\mathbf{P}^e|$  and  $|\mathbf{P}^p|$  back to unity again and again at intervals  $2\pi/\omega$ . Generally, however, a two-spin system has four energy eigenvalues and six eigenfrequencies, as detailed in Sec. III.G. Regardless of details, its polarization vector  $\mathbf{V}$  will never again return to its initial orientation, with  $|\mathbf{P}^e| = |\mathbf{P}^p| = 1$  and  $\mathcal{C}^{ep} = 0$ , unless all six frequencies are commensurable.

Both of the circumstances indicated above may be expected to operate dramatically in large aggregates of particles. The frequency spectrum of such systems is extremely dense, forming practically a continuum of incommensurable elements. The number of nonzero components of their polarization vectors  $\mathbf{V}$ , initially small, will generally increase irreversibly, spreading through the uncountable number of dimensions that are accessible to  $\mathbf{V}$  in the absence of special conservation laws.

#### F. Vanishing of polarization components through symmetry

We have seen in Sec. II how spin polarization components orthogonal to a magnetic field vanish because of axial symmetry in a state of thermal equilibrium. In the two-spin problem studied in this section, the initial state itself, Eq. (3.4'), is defined as having axial symmetry about  $\hat{z}$ , a symmetry preserved in its subsequent evolution

governed by the scalar Hamiltonian (3.14). The ten components of the polarization vector  $\mathbf{V}$  that lack this axial symmetry must accordingly vanish. [The five components with axial symmetry are  $P_z^e, P_z^p$ , the scalar (3.11a), the  $z$  component of the vector (3.11b), and the 0 component of the tensor (3.11c).] The same would hold, of course, for a pair of spins in thermal equilibrium in a magnetic field  $B\hat{z}$ .

If the initial spin orientations  $\mathbf{P}^e$  and  $\mathbf{P}^p$  had not been parallel, i.e., if these vectors were oriented as in the diagram of Fig. 3, the polarization would no longer be axial but would retain symmetry under reflection through the plane  $(\mathbf{P}^e, \mathbf{P}^p)$ , and all components of  $\mathbf{V}$  odd under this reflection would vanish. The reflection symmetry would persist in the course of time as the symmetry plane precesses about  $\mathbf{P}^e + \mathbf{P}^p$ .

These examples indicate that most components of generalized polarization vectors are likely to vanish for symmetry reasons, as anticipated in Sec. I. This property emerges, however, only if the components are identified by appropriate symmetrization, as was done in Sec. III.B. Consider, for instance, a large aggregate of matter which is macroscopically homogeneous, i.e., invariant under translations much larger than atomic or other structural inhomogeneities. This homogeneity is exploited by Fourier expansion of the state parameters analogous to (3.6). Homogeneity implies that all Fourier components with sufficiently large wavelength should vanish, in the absence of external fields with nonzero Fourier components of the same wavelength. Mean-square values of such components however, need not vanish because of thermal noise; their magnitude is implicit in the thermal factor of the density operator, analogous to (2.26), i.e.,  $\exp(-H/kT)/\text{Tr}[\exp(-H/kT)]$ . Considerations of this type generally underlie the formulation of most treatments of large aggregates but are implied by the description of *ad hoc* models rather than stated explicitly.

#### G. Time dependence with a nondegenerate spectrum

The Hamiltonian (3.14) utilized in Sec. III.C has three degenerate eigenstates with  $F = 1$  and  $M = 1, 0, -1$ . The evolution of a bound state of the spin pair emerges in its full generality when this degeneracy is lifted by additional terms in the Hamiltonian. This effect is achieved typically by introducing a magnetic field  $B\hat{z}$ , which changes (3.14) into

$$H = b\sigma^e \cdot \sigma^p - \frac{1}{2}\hbar(\gamma_e \sigma_z^e \mathbb{1}^p + \gamma_p \mathbb{1}^e \sigma_z^p)B, \quad (3.25)$$

where  $\gamma_e$  and  $\gamma_p$  indicate the gyromagnetic ratios of the particles.

Since this Hamiltonian is no longer invariant under the particle permutation  $\mathcal{P}^{ep}$ , we consider first its weak-field (Zeeman) limit

$$H_Z = b\sigma^e \cdot \sigma^p - \frac{1}{2}\gamma_Z \hbar(\sigma_z^e \mathbb{1}^p + \mathbb{1}^e \sigma_z^p)B, \quad (3.25')$$

where  $\gamma_Z$  is Lande's effective gyromagnetic ratio of the pair in its triplet states ( $F = 1$ ). Substitution of this Ham-

iltonian on the left of Eq. (3.10') replaces the frequency  $\omega$  on the right of (3.10') and in the following equations by  $\omega \pm \gamma_Z B$ , when applied to  $x$  or  $y$  components of  $\mathbf{M}^\pm$  or other vectors. (The operators  $\sigma_z^e$  and  $\sigma_z^p$  commute with  $M_z^\pm$  and hence don't affect its time dependence.) The single frequency  $\omega$  is thus replaced by a Zeeman triplet of frequencies. The second and fourth terms of the density matrix (3.13), which remained constant in Eq. (3.16), also become time dependent under the influence of the magnetic field, precessing with frequency  $\gamma_Z B$ , because they do not commute with the  $(\sigma_z^e + \sigma_z^p)$  term of (3.25'). The Fourier spectrum of  $\rho^{ep}(t)$  thus consists of the four frequencies  $\omega$ ,  $\omega \pm \gamma_Z B$ , and  $\gamma_Z B$ . One of these frequencies,  $\gamma_Z B$ , is still degenerate, because it corresponds to transitions between  $M_F=0$  and either  $M=1$  or  $M=-1$ .

Returning now to the Hamiltonian (3.25), we note that  $M$  remains a good quantum number, because (3.25) retains axial symmetry about  $\hat{z}$ . The quantum number  $F$ , instead, remains good only for  $M = \pm 1$  but has to be replaced by a new label, which we call  $\bar{F}=(0,1)$ , and which reduces to  $F$  in the weak-field limit or for  $M = \pm 1$ . The four well-known eigenvalues of (3.25) are (Feynman *et al.* 1965, Vol. III, Sec. 12.4)

$(\bar{F}, M)$	$\bar{E}(\bar{F}, M)$
$(1, \pm 1)$	$b - \frac{1}{2} \hbar (\gamma_e - \gamma_p) B,$
$(1, 0)$	$-b + \{4b^2 + [\frac{1}{2} \hbar (\gamma_e - \gamma_p) B]^2\}^{1/2},$
$(1, -1)$	$b + \frac{1}{2} \hbar (\gamma_e - \gamma_p) B,$
$(0, 0)$	$-b - \{4b^2 + [\frac{1}{2} \hbar (\gamma_e - \gamma_p) B]^2\}^{1/2}.$

(3.26)

The six distinct differences between pairs of these eigenvalues will appear as frequencies in the Fourier spectrum of the density matrix  $\rho^{ep}(t)$ . In Sec. III.C,  $\rho^{ep}(t)$  was obtained by simply inserting a factor  $\exp(\pm i\omega t)$  into the terms of  $\rho^{ep}(0)$  with  $F$ -shifting operators  $\mathbf{M}^\pm$ . That procedure is no longer immediately applicable here, because the operators  $\mathbf{M}^\pm$  had been selected on the basis of a classification of permutation symmetry,  $\mathcal{P}^{ep}$ , which does not apply to the Hamiltonian (3.25) or to its eigenvectors.

Extended application of the earlier procedure is achieved nevertheless by an artifice of broad significance, namely, by *mapping* the eigenvectors and eigenvalues of the lower symmetry Hamiltonian (3.25) onto those of a model Hamiltonian of maximal symmetry,  $H_S$ , with the same eigenvalues (3.26) but with *different eigenvectors*  $|F, M\rangle$ . The time-dependent matrix  $\rho_S^{ep}(t)$  will then be constructed for the model system providing its *Fourier expansion directly*. That is, each term of  $\rho^{ep}(t)$  will have a single time-dependent factor,

$$\exp\{-i[E(F', M') - E(F, M)]t/\hbar\}, \quad (3.27)$$

analogous to that of  $\rho(t)$  in Eq. (2.18). The time evolution of the actual spin pair may finally be obtained by the equivalence transformation

$$\rho^{ep}(t) = \langle \bar{F}' | F' \rangle \rho_S^{ep}(t) \langle F | \bar{F} \rangle, \quad (3.28)$$

where  $\langle \bar{F}' | F' \rangle$  is the unitary transformation that maps  $|\bar{F}M\rangle$  onto  $|FM\rangle$ . A more general framework for this procedure will emerge in Sec. V.

The construction of the model Hamiltonian  $H_S$  rests on the fact that the symmetrized set of Sec. III.B includes four commuting operators, which may be derived by linear combination from the basis of four eigenvectors,  $|FM\rangle\langle FM|$ . The four commuting operators have axial symmetry about  $\hat{z}$ , as the  $|FM\rangle\langle FM|$  also have, and serve to represent  $H_S$  in the form

$$H_S = \bar{a} \mathbb{1}^e \mathbb{1}^p + \bar{b} \sigma^e \cdot \sigma^p + \bar{c} \frac{1}{2} (\sigma_z^e \mathbb{1}^p + \mathbb{1}^e \sigma_z^p) + \bar{d} \frac{1}{2} (3\sigma_z^e \sigma_z^p - \sigma^e \cdot \sigma^p). \quad (3.29)$$

The four coefficients  $(\bar{a}, \bar{b}, \bar{c}, \bar{d})$  are then determined by equating the eigenvalues  $E(F, M)$  of  $H_S$ ,

$$\begin{aligned} (F, M) &= (1, 1), & (1, 0), & (1, -1), & (0, 0), \\ E &= \bar{a} + \bar{b} + \bar{c} + \bar{d}, & \bar{a} + \bar{b} - 2\bar{d}, & \bar{a} + \bar{b} - \bar{c} + \bar{d}, & \bar{a} - 3\bar{b}, \end{aligned} \quad (3.30)$$

to the  $\bar{E}(\bar{F}, M)$  of Eq. (3.26).

Our main task now is to identify the terms of the expression (3.13) of  $\rho^{ep}$  that will acquire the respective time-dependent factors (3.27) with the alternative sets of quantum numbers; allowing for permutations of primed and unprimed indices, there are 12 such distinct factors. Among the 16 terms of  $\rho^{ep}$ , four remain invariant in time, because their operators belong to the commuting set in the Hamiltonian (3.29). Most of the other terms have to be reassembled so that each of them changes just one pair  $(F, M)$  into a single  $(F', M')$ . The six components of  $\mathbf{M}^\pm$  are sorted out according to the  $M$ -raising (-lowering) properties of their components by setting

$$\begin{aligned} \mathbf{M}^+ &\equiv \{M_x^+ = -\sqrt{1/2}(M_x^+ + iM_y^+), \\ &M_z^+ = \sqrt{1/2}(M_x^+ - iM_y^+), M_z^+\} . \end{aligned} \quad (3.31)$$

$\mathbf{M}^-$  is sorted out accordingly. The  $(x, y)$  components of  $\sqrt{1/2}(\sigma^e \mathbb{1}^p + \mathbb{1}^e \sigma^p)$ , Eq. (3.9a), are similarly sorted out into  $\pm$  components and also combined with  $U_{\pm 1}^{(2)}$ , Eq. (3.8c), to yield

$$N_{\pm 1}^{\pm 1} = -\frac{1}{2} [\sigma_+^e (\mathbb{1}^p \pm \sigma_z^p) + (\mathbb{1}^e \pm \sigma_z^e) \sigma_+^p] \quad (3.32)$$

and the analogous  $N_{\pm 1}^{\pm 1}$ . Note how the  $N_{\pm 1}^{\pm 1}$  components contain projection operators  $(1 + \sigma_z)$  that exclude transitions to or from  $M = -1$ . The expression of  $\rho^{ep}$  in terms of these  $M$ -raising and -lowering operators includes, of course, similarly transformed combinations of the parameters  $\mathbf{P}^e$ ,  $\mathbf{P}^p$ , and  $\mathbf{P}^e \mathbf{P}^p + \mathcal{C}^{ep}$ . The time-dependent factors (3.27) are now allotted to the terms of  $\rho^{ep}$  according to their respective operators as indicated in the array

$(F, M)$	(1, 1)	(1, 0)	(1, -1)	(0, 0)
$(F', M')$				
(1, 1)		$N^+$	$U_{2+}^{(2)}$	$M_z^+$
(1, 0)	$N^+$		$N_+^+$	$M_z^+$
(1, -1)	$U_{2-}^{(2)}$	$N^-$		$M_z^+$
(0, 0)	$M^-$	$M_z^-$	$M_-^-$	

(3.33)

The procedure thus concluded may serve as prototype for the more extended applications to be envisaged in Sec. V.

**H. Summary**

Items developed in this section are listed here which appear to be relevant to larger systems. They are accordingly formulated with reference to a pair of spins and alternatively in more general terms.

(a) A complete set of operators for a pair of spins (or for a system consisting of two subsystems) is constructed according to (3.1) as direct product of complete sets for the separate spins (for the separate subsystems).

(b) The mean values of all the operators of the product set form a set of  $4^2$  ( $N^2$ ) parameters, Eq. (3.6), which characterizes the state of the system. The elements of this set, excluding unity, may be viewed as the components of a generalized polarization vector  $\mathbf{V}$  of a "Liouville" model space.

(c) The magnitude  $|\mathbf{V}|^2$  of this vector—i.e., the sum of squared moduli of its components—is restricted by Eq. (3.7') to  $\leq 15$  ( $N^2 - 1$ , where  $N$  is the number of mutually orthogonal pure states of the whole system). States of maximum  $|\mathbf{V}|^2$  are pure; "pure" and "mixed" states form together a "convex" set [Weyl, 1928, pp. 68–69 (pp. 78–79 in Eng. tr.)].

(d) Classification of the base operators and of the components of  $\mathbf{V}$  according to relevant symmetries is achieved by appropriate unitary transformations. Components of  $\mathbf{V}$  that vanish identically in states of interest because of symmetry conditions are thus identified, restricting the number of relevant nonzero parameters (Sec. III.F).

(e) In the Fourier representation of the time dependence of a density matrix,

$$\rho(t) = \sum_n \rho_n e^{-i\omega_n t}, \tag{3.34}$$

the coefficients  $\rho_n$  are components of the polarization vector  $\mathbf{V}$ . When the Hamiltonian has sufficient symmetry, the set of  $\rho_n$  may be constructed by symmetry analysis. Otherwise, an equivalent result is achieved by mapping the eigenstates of the system's Hamiltonian  $H$  onto those of a symmetric Hamiltonian  $H_S$  with the same eigenvalues as  $H$  (Sec. III.G).

(f) The squared magnitude of the polarization vector  $\mathbf{V}$  is conserved in the course of time. However, an increasing fraction of this magnitude may be transferred to components of  $\mathbf{V}$  that are not directly relevant to the phenomenon under study and may not even be accessible to realistic observation. The polarization would thus be effectively dissipated.

**IV. CORRELATIONS IN STATES WITH ZERO NET SPIN**

Correlation phenomena are particularly striking, as anticipated in Sec. I, when the spins (or other variables) of two subsystems average out to zero separately but their product is nevertheless nonzero. I illustrate such phe-

nomena in this section through examples in which the parameters ( $\mathbf{P}^e, \mathbf{P}^p$ ) of Eq. (3.5) vanish but the correlation tensor  $\mathcal{C}^{ep}$  does not.

The correlations are sampled by evaluating—theoretically or experimentally—the average product of the response of two detectors  $Q^e$  and  $Q^p$  sensitive to the respective spin orientations of the two particles. Each of these detectors may be represented as  $q\mathbf{1} + \mathbf{Q} \cdot \boldsymbol{\sigma}$  with  $q \geq |\mathbf{Q}|$ , according to Eq. (2.11), but we standardize here on eigenvalues of  $Q$  that do not exceed unity and average  $\frac{1}{2}$ , setting

$$Q^e = \frac{1}{2}(1^e + \mathbf{Q}^e \cdot \boldsymbol{\sigma}^e), \quad Q^p = \frac{1}{2}(1^p + \mathbf{Q}^p \cdot \boldsymbol{\sigma}^p), \tag{4.1}$$

$$(|\mathbf{Q}^e|, |\mathbf{Q}^p|) \leq 1.$$

Setting now  $\mathbf{P}^e = \mathbf{P}^p = 0$  in Eq. (3.5), we find that the mean value of  $Q^e Q^p$ , Eq. (3.2), yields

$$\langle Q^e Q^p \rangle = \frac{1}{4}(1 + \mathbf{Q}^e \cdot \mathcal{C}^{ep} \cdot \mathbf{Q}^p). \tag{4.2}$$

Sampling the value of  $\langle Q^e Q^p \rangle$  for various orientations of  $\mathbf{Q}^e$  and  $\mathbf{Q}^p$  maps out the correlation tensor  $\mathcal{C}^{ep}$  of a given state.

**A. Stationary state with spin quantum number  $F = 0$**

This state is represented by the antisymmetric spinor function  $\sqrt{1/2}(\alpha^e \beta^p - \beta^e \alpha^p)$ , where  $\alpha$  and  $\beta$  stand for "spin-up" and "spin-down," respectively. Evaluating the mean values of the nine operators  $\sigma^e \sigma^p$  with this wave function yields

$$\langle \sigma_i^e \sigma_j^p \rangle = -\delta_{ij}. \tag{4.3}$$

Thus we have

$$\begin{aligned} \rho_{F=0}^{ep} &= \frac{1}{4}(1^e 1^p - \sigma_x^e \sigma_x^p - \sigma_y^e \sigma_y^p - \sigma_z^e \sigma_z^p) \\ &= \frac{1}{4}(1^e 1^p - \boldsymbol{\sigma}^e \cdot \boldsymbol{\sigma}^p) \end{aligned} \tag{4.4}$$

and hence

$$\langle Q^e Q^p \rangle_{F=0} = \frac{1}{4}(1 - \mathbf{Q}^e \cdot \mathbf{Q}^p). \tag{4.5}$$

[Notice how the density matrix (4.4) clearly represents a projection operator, since the eigenvalues  $-3$  and  $1$  of  $\boldsymbol{\sigma}^e \cdot \boldsymbol{\sigma}^p$  yield  $1$  and  $0$  for the eigenvalues of  $\rho_{F=0}^{ep}$ .]

Peak response of the detector pair is achieved for  $\mathbf{Q}^e = -\mathbf{Q}^p$ ,  $|\mathbf{Q}^p| = 1$ , regardless of the orientation of the vector pair, as expected from the isotropy of our state. This peak response equals  $\frac{1}{2}$ , namely, the chance of observing the pair with any one orientation of  $\mathbf{Q}^e = -\mathbf{Q}^p$ ; an equal—complementary—response would be obtained for the same system by interchanging the orientations of  $\mathbf{Q}^e$  and  $\mathbf{Q}^p$ . A more characteristic property of this correlated state is that  $\langle Q^e Q^p \rangle$  vanishes when  $\mathbf{Q}^e$  and  $\mathbf{Q}^p$  are parallel and of unit magnitude. That is, even though the orientation of each separate spin is random, simultaneous observations of the two spins by "perfect" selectors  $|\mathbf{Q}^e| = |\mathbf{Q}^p| = 1$ , with parallel orientation is strictly ex-

cluded. This exclusion amounts to stating that our  $F=0$  state is orthogonal to any state with  $F=1$ .

**B. Stationary state with  $F=1$  and  $M=0$**

A triplet state with these quantum numbers is represented by the symmetric spinor function  $\sqrt{1/2}(\alpha^e\beta^p + \beta^e\alpha^p)$ , with reference to the electron-proton pair of Sec. III. This type of state is, of course, anisotropic, but it arises in the decay of isotropic (spinless) systems of odd parity such as pions, kaons, and parapositronium. The relative momentum  $\mathbf{p}$  of two particles or photons emitted in the decay provides the axis of reference for the magnetic quantum number  $M$  of the pair with  $F=1$ . The zero value of  $M$  then means that the pseudoscalar product  $\mathbf{F}\cdot\mathbf{p}$  vanishes.

In the following analysis of correlations we shall refer to the two spins as  $\sigma^e$  and  $\sigma^p$ , without implying that we are dealing with an electron-proton pair. Use of the permutation  $\mathcal{P}^{ep}$  will not imply identity of the particles or of their respective Hamiltonians; it merely reflects the isotropy of the source, which permits neither particle to be associated with any one direction of space. To see that  $\mathbf{P}^e = \langle \sigma^e \rangle$  and  $\mathbf{P}^p = \langle \sigma^p \rangle$  vanish, consider first that  $M = \frac{1}{2} \langle \sigma_z^e \mathbb{1}^p + \mathbb{1}^e \sigma_z^p \rangle = \frac{1}{2} (P_z^e + P_z^p) = 0$ , whence  $P_z^e = P_z^p = 0$ , because of symmetry under  $\mathcal{P}^{ep}$ . The components of  $\mathbf{P}^e$  and  $\mathbf{P}^p$  orthogonal to  $z$  also vanish because of axial symmetry about  $\hat{z}$ .

Correlation properties of our state also follow from its quantum numbers and symmetries. According to Sec. III.B,  $F=1$  implies eigenvalue unity of the scalar (3.8a),  $\sigma^e \cdot \sigma^p = 1$ . Symmetry under  $\mathcal{P}^{ep}$  implies that the mean value  $\langle \sigma^e \times \sigma^p \rangle$  vanishes. Furthermore,  $M^2 = \frac{1}{4} (\sigma_z^e \mathbb{1}^p + \mathbb{1}^e \sigma_z^p)^2 = 0$  implies that  $\sigma_z^e \sigma_z^p = -1$ . From this eigenvalue and from  $\sigma^e \cdot \sigma^p = 1$  follows the eigenvalue of one quadrupole component of (3.8c),  $U_0^{(2)} = \sqrt{1/6} (3\sigma_z^e \sigma_z^p - \sigma^e \cdot \sigma^p) = \sqrt{1/6} (2)$ . The mean values of the other quadrupole components,  $\langle U_{\pm 1}^{(2)} \rangle$  and  $\langle U_{\pm 2}^{(2)} \rangle$ , vanish, owing to axial symmetry about  $\hat{z}$ .

The density matrix is then

$$\rho_{F=1, M=0}^{ep} = \frac{1}{4} (\mathbb{1}^e \mathbb{1}^p + \sigma_x^e \sigma_x^p + \sigma_y^e \sigma_y^p - \sigma_z^e \sigma_z^p), \quad (4.6)$$

meaning that  $\langle \sigma_x^e \sigma_x^p \rangle = \langle \sigma_y^e \sigma_y^p \rangle = -\langle \sigma_z^e \sigma_z^p \rangle = 1$  and that  $\langle \sigma_i^e \sigma_j^p \rangle$  vanishes for all  $i \neq j$ . The response of our coincidence detector is accordingly

$$\langle Q^e Q^p \rangle_{F=1, M=0} = \frac{1}{4} (1 + Q^e \cdot Q^p - 2Q_z^e Q_z^p). \quad (4.7)$$

The anisotropy of this state thus manifests itself in its spin correlations. *Parallel* spin orientation,  $\mathbf{Q}^e = \mathbf{Q}^p$ , is again excluded, as in the  $F=0$  case, but *only* for  $\mathbf{Q}^e$  and  $\mathbf{Q}^p$  parallel to the  $z$  axis. *Opposite* orientation,  $\mathbf{Q}^e = -\mathbf{Q}^p$ , is instead excluded when these vectors are *orthogonal* to the  $z$  axis. Anisotropy was, of course, to be anticipated for any pure state with  $F=1$ , or anyhow with nonzero squared angular momentum.<sup>6</sup>

<sup>6</sup>A classification of all possible anisotropies of pure states with unit spin has been given in Fano (1968).

An isotropic mixed state with  $F=1$  can be constructed by incoherent superposition of three states with  $F=1$  and with the specification of  $M=0$  referred to three mutually orthogonal axes. Its density matrix is

$$\rho_{F=1, \text{isotr}}^{ep} = \frac{1}{4} (\mathbb{1}^e \mathbb{1}^p + \frac{1}{3} \sigma^e \cdot \sigma^p). \quad (4.8)$$

The detector response is then

$$\langle Q^e Q^p \rangle_{F=1, \text{isotr}} = \frac{1}{4} (1 + \frac{1}{3} Q^e \cdot Q^p), \quad (4.9)$$

which peaks for  $\mathbf{Q}^e = \mathbf{Q}^p$  regardless of their direction. Peak response of this detector is only  $\frac{1}{3}$ , and its minimum  $\frac{1}{6}$ , showing that isotropy implies a weaker correlation.

**C. Correlation of photon pairs**

Direct observation of correlations is more readily achieved and transparent for the polarization of photon pairs than for the spin orientation of pairs of particles, because radiation propagates readily and without disruption over laboratory distances. Coincidence experiments with photons are particularly striking when their source and each of its constituents are manifestly isotropic. The response of a pair of detectors facing the source from opposite directions, as in Fig. 4, is then manifestly independent of the detectors' joint rotation about the source center or about their common axis.

Conservation of angular momentum about the common axis of propagation of a photon pair has immediate relevance to the correlation of circular polarizations. *Equal helicity* of circularly polarized photons propagating in *opposite directions* is then required for their angular momenta to cancel. Thus one may anticipate finding a photon pair in states represented, with reference to "right" or "left" circular polarizations by  $|R_1 R_2\rangle$  or  $|L_1 L_2\rangle$ , or by their superpositions, whereas  $|R_1 L_2\rangle$  or  $|L_1 R_2\rangle$  would imply a total momentum about the axis of  $\pm 2\hbar$ , inconsistent with the assumed isotropy of the emission.

A second consideration concerns parity under inversion at the center of the source. This operation reverses the

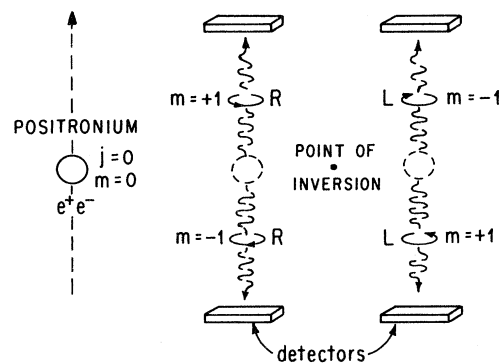
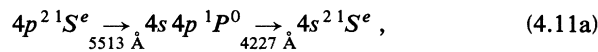


FIG. 4. Positronium annihilation and two-photon coincident detection, showing the polarization reversal under inversion at a center. (The two polarization diagrams are shifted off-center for clarity.)

photon helicities as shown in Fig. 4, thus interchanging the states  $|R_1R_2\rangle$  and  $|L_1L_2\rangle$ . A process of two-photon emission by transition between atomic eigenstates of parity must then result in an eigenstate of two-photon parity,

$$\sqrt{1/2}\{ |R_1R_2\rangle \pm |L_1L_2\rangle \}, \quad (4.10)$$

where the sign reflects the parity of the source transition. Two sources with opposite parity have been studied experimentally, one of them optical from calcium (Ca) vapor,



and the other in the  $\gamma$ -ray range from the annihilation of positronium (Ps) in its ground-state singlet,



$$\sqrt{1/2}(|\sqrt{1/2}(\hat{x}_1 + i\hat{y}_1), \sqrt{1/2}(\hat{x}_2 + i\hat{y}_2)\rangle + |\sqrt{1/2}(\hat{x}_1 - i\hat{y}_1), \sqrt{1/2}(\hat{x}_2 - i\hat{y}_2)\rangle)$$

$$= \sqrt{1/2}(|\hat{x}_1\hat{x}_2\rangle - |\hat{y}_1\hat{y}_2\rangle) = \sqrt{1/2} \left[ \left| \frac{\hat{x}_1 + \hat{y}_1}{\sqrt{2}}, \frac{\hat{x}_2 - \hat{y}_2}{\sqrt{2}} \right\rangle + \left| \frac{\hat{x}_1 - \hat{y}_1}{\sqrt{2}}, \frac{\hat{x}_2 + \hat{y}_2}{\sqrt{2}} \right\rangle \right], \quad (4.12a)$$

and

$$\sqrt{1/2}(|\sqrt{1/2}(\hat{x}_1 + i\hat{y}_1), \sqrt{1/2}(\hat{x}_2 + i\hat{y}_2)\rangle - |\sqrt{1/2}(\hat{x}_1 - i\hat{y}_1), \sqrt{1/2}(\hat{x}_2 - i\hat{y}_2)\rangle) = i\sqrt{1/2}(|\hat{x}_1\hat{y}_2\rangle + |\hat{y}_1\hat{x}_2\rangle). \quad (4.12b)$$

The expressions on the right show that linear polarization detectors will pick up the photon pair in coincidence when laid parallel to one another in case *a*, but when orthogonal in case *b*. (Linear polarization of  $\gamma$  rays is observed by detecting each photon *after* an initial Compton scattering, the scattering plane being preferentially orthogonal to the linear polarization.)

This important phenomenon is discussed in Feynman's *Lectures* (Feynman *et al.* 1965, Vol. III, pp. 18.5–18.9) with particular reference to the Einstein-Podolsky-Rosen paradox. Einstein *et al.* (1935) had developed the treatment outlined here to stress how quantum mechanics leads to the (seemingly) absurd result that the setting of detector 1 serves to predict the response of the distant detector 2, a response that would itself be random if disconnected from 1. The paradox stems from failure to realize that the polarization correlation is a property of the photon pair, unrelated to those of single photons. In fact, an analogous observation can be made on the hands of one person: Observation of just one hand may show it to be a right or left hand with equal probability, but once a hand is identified as the right hand of a person, the other hand is predictably the left one. The 1950 experiment on annihilation verified the quantum-mechanical prediction clearly, but discussions and ever more accurate experimental tests of this paradox still linger on (Clauser and Shimony, 1978; Aspect *et al.*, 1982).

The correspondence between the polarization of photons and of particle spins may be established by treating the pairs of coefficients of  $(\hat{x}_1, \hat{y}_1)$  and of  $(\hat{x}_2, \hat{y}_2)$  in Eq.

(It is essential here that the initial Ps state and the vacuum after annihilation have opposite parity.) The optical experiment requires an adequate concentration of excited Ca atoms in a specific state, which was achieved only by laser technology (Freedman and Clauser, 1972). The annihilation experiment is facilitated by the low background of  $\gamma$ -ray detectors and was performed much earlier (Wu and Shaknov, 1950).

To examine the implications of parity for the polarization analysis of the two processes (4.11) we replace the symbols *R* and *L* by explicit expressions of polarization vectors referred to right-handed triads  $(\hat{x}_1 = \hat{x}_2, \hat{y}_1 = -\hat{y}_2, \hat{z}_1 = -\hat{z}_2)$ , with their  $\hat{z}$  axes pointed from the source to each of the two detectors. The alternative states (4.10) are thus represented, respectively, by

(4.12) as forming a spinor analogous to that of Eq. (2.2), as detailed, for example, in Fano (1949). Indicating these pairs of coefficients by  $(\alpha^1, \beta^1)$  and  $(\alpha^2, \beta^2)$  maps the two states (4.12a), (4.12b) onto the two-spin states  $\sqrt{1/2}(\alpha^1\beta^2 \mp \beta^1\alpha^2)$ , respectively. The corresponding density matrices are represented by (4.4) and (4.6), with quantum numbers  $(F=0, M=0)$  and  $(F=1, M=0)$  and with detector correlations (4.5) and (4.7), respectively.<sup>7</sup>

## V. EXTENSIONS

I outline here how the treatment of a pair of spins may serve as a model for the treatment of larger, even very large, systems. In a first step the representation of spin- $\frac{1}{2}$  states will be extended to the states of a particle with higher spin (Sec. V.A). Alternative mappings of single multilevel systems or of combinations of subsystems will then be considered (Sec. V.B). An illustration of experimental Fourier analysis of time-dependent correlations of atomic states follows in Sec. V.C. The final section, V.D, will indicate how one approaches the representation of relevant variables in very large systems subject to dissipation and relaxation effects.

<sup>7</sup>The brief treatment of this topic in Sec. 4d of Fano (1957) was *incorrect*. It amounted to interchanging (4.12b) with (4.12a), thus mapping it onto the density matrix (4.4) instead of (4.6).

### A. Parameters of spin- $j$ states<sup>8</sup>

The degenerate ground level of an atom or nucleus with spin  $j$  has multiplicity  $2j+1$ . Removal of this degeneracy by application of a weak magnetic field separates out  $2j+1$  nondegenerate levels,  $|jm\rangle$ , with  $-j \leq m \leq j$ . Further application of fields of higher multipolarity introduces uneven spacings of the energy levels  $E_m$ , but the index  $m$  may nevertheless serve as a label.

The role played in Sec. II by the set of four operators  $\{1, \sigma\}$  is performed for spin  $j$  by a set of  $(2j+1)^2$  orthonormal operators  $\{U_q^k\}$  with  $0 \leq k \leq 2j$  and  $-k \leq q \leq k$ . Orthonormalization of this set in analogy to spin  $\frac{1}{2}$  is achieved by the definition

$$U_q^k = \sum_m \sum_{m'} |jm\rangle \langle jm'| (-1)^{j-m'} (jmj - m' | jjkq) \times (2j+1)^{1/2}, \quad (5.1)$$

in which the symbol in parentheses is a Wigner coefficient. The operators (5.1) are non-Hermitian, being analogous to  $\sqrt{1/2}(\sigma_x \pm i\sigma_y)$ ; their orthonormality is accordingly represented by the relation

$$\text{Tr}(U_q^k U_{q'}^{k'\dagger}) = (2j+1) \delta_{kk'} \delta_{qq'}, \quad (5.2)$$

which is implied by the orthogonality of the matrix  $(jm, jm' | jjkq)$ . Note that  $U_0^0 \equiv 1$  and that  $\text{Tr}(U_q^k) = (2j+1) \delta_{k0} \delta_{q0}$ .

The operators  $U_q^k$  transform under coordinate rotations like spherical harmonics  $Y_{lm}(\theta, \varphi)$  with  $l=k$  and  $m=q$ . External fields that remove the degeneracy of  $|jm\rangle$ , preserving axial symmetry about  $\hat{z}$ , are represented by superpositions of the subset  $\{U_0^k\}$ , with  $q=0$ . The operators of this subset commute with one another, being superpositions of  $|jm\rangle \langle jm|$ , according to (5.1), just as the four operators in the model Hamiltonian (3.29) commute.<sup>9</sup>

The set of mean values  $\langle U_q^k \rangle$  identifies the state of a spin- $j$  particle, as the components of  $\langle \sigma \rangle$  do for a particle of spin  $\frac{1}{2}$ . The polarization index, Eq. (3.7'), extends into

$$\sum_{k=1}^{2j} \sum_{q=-k}^k |\langle U_q^k \rangle|^2 \leq (2j+1)^2 - 1 = 4j(j+1), \quad (5.3)$$

where the equality holds for pure states and the  $<$  sign for mixed states. The density matrix of the state is represented as a linear combination of the operator set  $\{U_q^k\}$ , with coefficients  $\langle U_q^{k\dagger} \rangle$ . Each operator  $U_q^k$  with

$q \neq 0$  acts to raise (lower) the quantum number  $m$  by  $q$  ( $-q$ ) units, as the spin- $\frac{1}{2}$  operator  $\sqrt{1/2}(\sigma_x + i\sigma_y) \equiv -U_1^1$  raises the  $m$  value from  $-\frac{1}{2}$  to  $\frac{1}{2}$ . Accordingly, the matrix  $(m+q | U_q^k | m)$  has  $2j - |q|$  nonzero elements with values of  $m$  ranging from  $-j$  to  $j-q$ .

Operators whose matrix has a single nonzero element, as is the case for the  $j = \frac{1}{2}$  operator  $U_1^1 = -\sigma_+$ , raise one index  $m$  by  $q$  units to  $m+q$  and will be indicated accordingly, by  $U^{qm}$ . Each of them is constructed, for  $j > \frac{1}{2}$ , by a superposition

$$(m+q | U^{qm} | m') = \sum_{k=|q|}^{2j} a_{mk}(m'+q | U_q^k | m') = \delta_{m', m+q}. \quad (5.4)$$

This construction serves to identify Fourier components of time dependence, as the construction of the array (3.33) did in Sec. III.G, since (5.2) implies that

$$\exp(iHt/\hbar) U^{qm} \exp(-iHt/\hbar) = \exp[i(E_{m+q} - E_m)t/\hbar] U^{qm}. \quad (5.5)$$

We have thus introduced a new base set of operators, each of which has the single effect of changing one specific stationary state,  $|jm\rangle$ , into another specific state,  $|j, m+q\rangle$ . Any operator can be represented as a superposition of elements of this base set. The time dependence of each operator of this set is represented by a single exponential factor in the Heisenberg representation of Eq. (5.5).

### B. Mapping of $N$ -level systems and of correlated subsystems

Even as the states of any two-level system can be set in one-to-one correspondence to those of a spin- $\frac{1}{2}$  particle (Sec. II.E), so can the states of any  $N$ -level system be mapped onto those of a particle with spin  $j = \frac{1}{2}(N-1)$ . More specifically, each energy eigenstate  $|n\rangle$  of the  $N$ -level system is set in correspondence with the state  $|jm\rangle$  of a particle subjected to axisymmetric fields such that the energy of  $|jm\rangle$  equals  $E_n$ . The parametrization described in Sec. V.A is thus applicable, in effect, to the states of any quantum system.

This general representation of quantum states rests on the isomorphism of vector spaces with equal dimensions, as outlined in Fano (1957). It has not been applied extensively, probably because the multipole parameters  $\langle U_q^k \rangle$  of a spin- $j$  particle are much less familiar than the vector  $\langle \sigma \rangle$  of a particle with spin  $\frac{1}{2}$ . Current interest in quantum-optical systems with three or more levels seems, however, to draw attention in similar directions (Hioe and Eberly, 1981). Use of the base set of operators (5.5) which oscillate with a single frequency might prove attractive.<sup>10</sup>

<sup>8</sup>This parametrization dates from the 1950s and has been utilized extensively in the processes indicated in the introduction to Sec. III.

<sup>9</sup>The subset  $\{U_0^k\}$  represents  $2j+1$  linearly independent functions of energy  $H$ , if the base set  $|jm\rangle$  represents nondegenerate stationary states. In the case of degeneracy, one or more combinations of the  $\{U_0^k\}$  are nontrivial constants of the motion.

<sup>10</sup>This Fourier-analysis procedure, which starts from diagonalization of the Hamiltonian, seems more transparent than the extension of the precession Eq. (2.24) developed by Fano (1964).



Remarkably, a base set of operators equivalent to the  $U_q^k$  of Sec. V.A had been introduced by Cartan long before the quantum theory of angular momentum. The goal was to develop standard unitary irreducible representations of order  $N$  for semisimple groups. A key point lay in the construction of the initial set of  $N$  commuting operators  $U_0^k$ , whose eigenvalues identify each irreducible representation and whose joint eigenvectors correspond to our energy eigenstates  $|jm\rangle$  with  $j = \frac{1}{2}(N-1)$  and  $-j \leq m \leq j$ . The next step was to complement the  $U_0^k$  by constructing the complementary set of  $2j(2j+1)$   $m$ -raising (or -lowering) operators equivalent to the  $U_q^k$  with  $q \neq 0$ . This subject has been reviewed by Racah (1963) in the context of quantum-mechanical applications. The mapping of the four energy eigenstates  $|\bar{F}M\rangle$  in Sec. III.G, onto the four eigenstates  $|FM\rangle$  of the superposition  $H_S$  of four commuting operators, in effect utilized Cartan's theorems.

Note, however, that elements of the base sets  $|\bar{F}M\rangle$  or  $|FM\rangle$  are distinguished by alternative values of *both* of their indices in contrast to the set  $|jm\rangle$ , where  $m$  alone distinguishes the elements, while  $j$  labels the set. Base sets of eigenstates with different structure may thus be used profitably in different applications. The structure of sets of base operators varies accordingly. Indeed, the two-spin treatment of Sec. III utilized a sequence of base sets of states and operators: direct product sets of states,  $|\frac{1}{2}m^e\rangle|\frac{1}{2}m^p\rangle$  and of operators, Eq. (3.1'), were used at the outset. Symmetrization of these products under space rotations led then to  $|FM\rangle$  and to the operators (3.8). The operator array (3.33) was finally constructed. Flexibility is thus stressed for adapting the formalism to specific tasks.

For example, the four orthogonal states  $|FM\rangle$  of Sec. III.G could have been mapped onto the set  $|jm\rangle$  of a single particle of spin  $j = \frac{3}{2}$ . This mapping would have homogenized the set at the price of wiping out the classifications by parity under the permutation  $\mathcal{P}^{ep}$  and according to the zero-field energy splitting by the coupling  $b\sigma^e \cdot \sigma^p$ . The parity classification has been similarly preserved in the study of the  $|nlm\rangle$  manifold of states of atomic H with  $n=2$ , which is isomorphic to the  $|FM\rangle$  set of Sec. III.G (Gabrielse, 1980).

Another variant in the mapping of states and operators has emerged from the symmetry analysis of correlations between the levels of two Zeeman multiplets coupled by laser optical transitions (Baer, 1978). Energy eigenstates of the two multiplets are indicated by  $|j_a m_a\rangle$  and  $|j_b m_b\rangle$ , respectively, the energy splitting between  $a$  and  $b$  levels being optical, between  $m_a$  and  $m'_a$  at radio frequency. A base array of operators is indicated by

$$\left\{ \begin{array}{l} |j_a m_a\rangle \langle j_a m'_a| \quad |j_a m_a\rangle \langle j_b m'_b| \\ |j_b m_b\rangle \langle j_a m'_a| \quad |j_b m_b\rangle \langle j_b m'_b| \end{array} \right\}. \quad (5.6)$$

Operators of the two blocks along the diagonal of this array oscillate at radio frequency in the Heisenberg representation and may be replaced by multipole operators  $\{U_{q_a}^{k_a}\}$  and  $\{U_{q_b}^{k_b}\}$ , respectively, in accordance with Eq.

(5.1). Interest centers, however, on the correlations oscillating at optical frequencies which correspond to the operators in the off-diagonal blocks of (5.6). Analysis according to rotational symmetry replaces these operators with two adjoint sets  $\{U_{q_{ab}}^{k_{ab}}\}$  and  $\{U_{q_{ba}}^{k_{ba}}\}$  constructed analogously to (5.1) but restricted by  $|j_a - j_b| \leq (k_{ab}, k_{ba}) \leq j_a + j_b$ .

### C. Observation of time-dependent correlations

The combination of optical and radio-frequency oscillations of the correlations corresponding to the operators in the array (5.6) can be displayed experimentally. This could be done by the study of photon echoes contemplated by Baer (1978). A more direct approach analyzes the light emission by atoms in flight.

A beam of atoms, molecules or ions excited within a narrow region of space—e.g., by collision with another beam—and traveling thereafter at speeds of  $10^7$ – $10^9$  cm/sec emits light during its further flight. Variations of light intensity and of its directional and polarization distributions along this flight are readily measured and Fourier analyzed (Fig. 5). This analysis provides direct

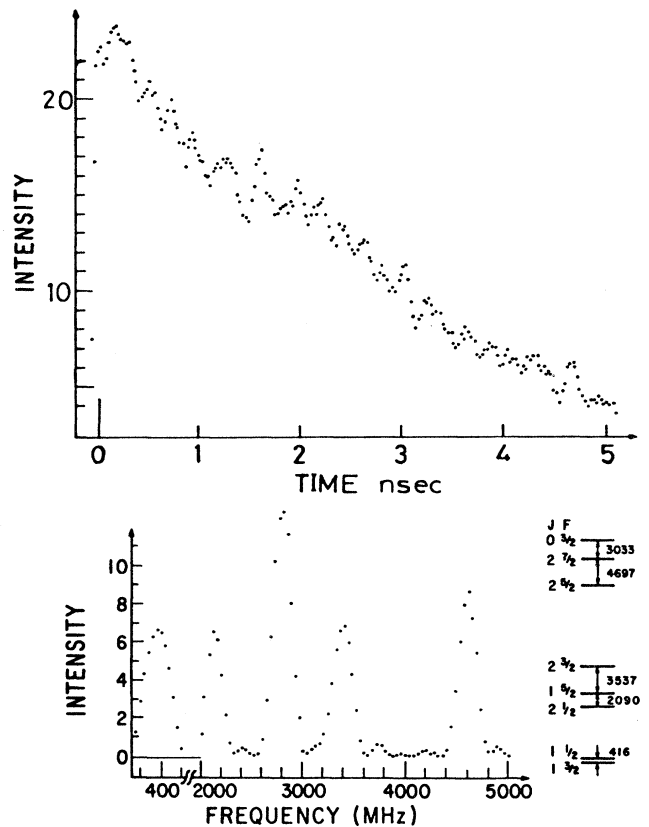


FIG. 5. Intensity decay curve of a line of the Li II spectrum and its Fourier transform (Berry *et al.*, 1973). Note the construction of hyperfine structure levels.

evidence on the correlated motion of atomic subunits.

The emission of light results from high-frequency oscillations ( $\sim 10^{15}$  Hz) of *optical* electron currents within an atomic system; its excitation generally involves similar currents. Accordingly, the observed radio-frequency variations of light emission reflect comparatively slow variations of the directional and/or intensity distribution of high-frequency orbital currents. Such variations are indeed expected to accompany the precession of the orbital angular momentum about the total angular momentum, which alone remains constant. The precession, induced by coupling with electron and nuclear spins, generates spin-current correlations of the very type described in Sec. III.

The analysis of the light emitted by beams of excited atoms has been discussed in some detail by Fano and Macek (1973), treating separately two steps of the observation process. Section II of this reference deals with the connection between the response of a detector, of given position and polarization setting with respect to the source, and the relevant parameters of the atomic source. These parameters concern the source orientation, i.e., its mean orbital momentum  $\langle \mathbf{L} \rangle$ , and its alignment, i.e., the mean value of a quadratic form in  $\mathbf{L}$  analogous to the expressions (3.8c). Section III of the same paper, the most relevant to the present subject, describes variations of the parameters that result primarily from oscillatory exchanges of orientation and alignment between the orbital motions and the electron and nuclear spins. Such transfers of polarization among different constituents are substantially equivalent to the exchanges between the orientation of different particles treated in Sec. III and elsewhere (e.g., Fano and Macek, 1973).

#### D. Correlations in large systems and their dissipation

The spin-resonance phenomena have served as a prototype for the analysis of correlations in large aggregates of matter. Attention is directed in these phenomena to the few variables that are observed directly. These variables are usually components of the mean orientation  $\mathbf{P}$  of an assembly of identical particles with spin, e.g., of electrons or protons, embedded in a material sample and subjected to a magnetic field. The influence of correlations between the spin variables and all the variables in the surrounding matter is then treated collectively.

One thus considers a small set of operators  $\{1^s, U_i^s\}$ , which represents the "system" of variables of interest and which is complete in the sense that the product of any two of its elements belongs to the set. A second large and complete set,  $\{1^m, \Phi_\alpha^m\}$ , represents the variables of the "medium." An array analogous to (3.1') combines the two sets:

$$\begin{pmatrix} 1^s 1^m & 1^s \Phi_\alpha^m \\ U_i^s 1^m & U_i^s \Phi_\alpha^m \end{pmatrix}. \quad (5.7)$$

The interaction between system and medium can be

represented as a superposition of  $U_i^s \Phi_\alpha^m$ . The  $U_i^s$  and  $\Phi_\alpha^m$  may be selected to oscillate with a single frequency in the Heisenberg representation.

Correlations of "system" and "medium" variables, represented by mean values  $\langle U_i^s \Phi_\alpha^m \rangle - \langle U_i^s \rangle \langle \Phi_\alpha^m \rangle$  according to (1.1), tend to entangle the time dependence of all the variables. In fact, however, the system's variables  $\langle U_i^s \rangle$  can be singled out and measured quasi-independently of the medium in many realistic phenomena. This very fact implies that the effect of correlations is circumscribed in practice and amenable to description by a few parameters.

Bloembergen (1948) pointed out, in essence, that the operators  $\Phi_\alpha^m$  in (5.7), when averaged over the state of the medium, act upon the system as additional external fields. One field component may have a steady nonzero value, while additional ones fluctuate as a manifestation of thermal noise. The fluctuating nature of these components limits their net effect. Wangsness and Bloch (1953) developed a more detailed analysis of the interaction between system and medium. Each variable of the system was seen to act on the medium by "polarizing" it in the sense of Sec. III. The key point of this analysis is that the polarization spreads quickly through the multitude of variables  $\Phi_\alpha^m$  as anticipated in Sec. III.E. Little of it thus remains in the few elements of the set  $\{\Phi_\alpha^m\}$  that can effectively react on the system's  $\{U_i^s\}$ . The net effect of this reaction can be represented in terms of friction parameters, which tend to draw the system into thermal equilibrium with the medium, *provided* the "memory time" of the medium polarization is short compared to the rates of evolution of the system of interest.

Operators  $U_i^s$  that oscillate with a single frequency of the system's Hamiltonian  $H^s$  are readily seen to relax toward a zero mean value under the influence of interactions with the medium. Their mean values would average to zero in the course of time regardless of such interactions. Weak and even slowly fluctuating interactions then suffice to dephase the oscillations of these  $U_i^s$ , whereby destructive interference brings their very amplitude to zero. Relaxation is instead slower for the mean values of the small subset of operators  $U_i^s$  that are time independent, like the  $\{U_0^k\}$  of Sec. V.A, because their mean values depend on the occupation of different energy levels. Relaxation to equilibrium thus requires discrete exchanges of energy between the system and the medium, corresponding to the eigenvalue spectrum of  $H^s$ . These exchanges are mediated by a small subset of operator products  $U_i^s \Phi_\alpha^m$  and accordingly proceed at a slower rate. The occurrence of two different relaxation times, called  $T_1$  for longitudinal and  $T_2$  for transverse components of the average spin orientation in a magnetic field, was recognized in Bloch's (1946) original paper on magnetic resonance and is essential to all analogous phenomena.

Let us return now to the central feature of the correlations between system and medium, namely, that the polarization of the medium spreads rapidly through its many variables. This phenomenon was visualized in Sec. III.E as the likely result of the polarization vector  $\mathbf{V}$ 's evolving

throughout the whole model space accessible to it with a broad and dense spectrum of frequencies whose superposition in effect yields an aperiodic motion. Departures from this likely behavior are known, however, in which special circumstances bring the vector  $\mathbf{V}$  back to the vicinity of an earlier direction. Such behavior has actually been observed in the evolution of complex systems of moderate size and is known in statistical mechanics as a "Poincaré cycle" or "Poincaré recurrence." The generally observed smooth relaxation of variables in magnetic resonance and analogous processes implies that such recurrences do not, in fact, happen in extended media within the duration of laboratory experiments. That is, the superposition of a very dense spectrum of frequencies appears actually to dissipate the polarization impressed upon the medium by the system of interest.

Even though the very large number of variables of a medium is probably sufficient to account for the observed dissipation of correlations, a theoretically more cogent factor emerges upon considering that this number of variables is actually infinite. Indeed, a portion of matter could be regarded as finite only when isolated from any mechanical, thermal, or radiative interaction with other matter. Specification of the state of any system with infinitely many variables requires additional conditions to be spelled out, which exclude the effect of additional sources of perturbation at infinite distance. These conditions introduce in Hamiltonian formalisms imaginary parameters that would otherwise be alien to it, thus providing the ultimate analytical basis for the occurrence of irreversibility in statistical mechanics (Zwanzig, 1960). The contrasting behavior of finite and infinite systems is readily illustrated by analytical models.

As mentioned above, the dissipation of spin polarization into the surrounding medium was represented by relaxation coefficients in Bloch's original differential equations for magnetic resonance. More generally, however, relaxation effects are represented by the decay of "correlation functions" of the form  $\langle A(t)B \rangle$  in the course of time. Here  $A$  and  $B$  are operators in the Heisenberg representation,  $A(t) = \exp(iHt/\hbar)A \exp(-iHt/\hbar)$ , and the correlation bears on values of  $A$  determined at a time  $t$  later than those of  $B$ . (The name "autocorrelation" applies when  $A$  and  $B$  coincide.) Interactions with the medium included in the Hamiltonian  $H$  are responsible for the "short memory" of the correlation functions. The Bloch parameters  $T_1$  and  $T_2$  were expressed by Bloembergen (1948) in terms of the autocorrelation of the magnetic field acting on a spin *within the medium*, evaluated in the limit  $t \rightarrow \infty$ . The point is that only the limit value matters, regardless of the time dependence of the correlation function, provided that the limit is approached adequately within a time interval much shorter than is required for spin precession due to the externally applied field.<sup>11</sup>

Let us note, finally, that correlation functions themselves constitute the centerpiece of studies that aim at unraveling detailed aspects of single collisions from the aggregate dissipation that results from multiple interactions with a medium. A typical example is afforded by the analysis of optical line profiles which are represented analytically by the Fourier transform of an autocorrelation function,  $I(\omega) = \int_0^\infty dt e^{-i\omega t} \langle z(t)z \rangle$ , where  $z$  indicates the mean displacement of atomic electrons from their average position. The "pressure broadened" profile  $I(\omega)$  depends both on experimental and single-collision parameters and on the averaging over the thermal parameters of the environment. Recent studies [Alford *et al.*, (1983), Burnett *et al.* (1982), Klerber *et al.* (1983), and references therein] have made considerable progress in sorting out the effects of different origin.

#### ACKNOWLEDGMENTS

This article originated from a graduate course presented at The University of Chicago in 1980 and again in 1981 at the Graduate School of the Chinese Academy of Sciences. The support of these institutions is gratefully acknowledged, as well as support of background research by the U.S. Department of Energy, Office of Basic Energy Sciences.

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<sup>11</sup>The term *relaxation* has also been applied to the reduction of spin polarization (or analogous parameters), due to coupling to a nuclear spin or other internal variable of atomic system of limited size (Lewis and Wheeler, 1977). In this case, the polarization transfer is basically reversible, and the relevant correlation function is periodic, as stressed by Fano and Macek (1973).

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