Stochastic Dynamics of Quantum-Mechanical Systems

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The most general dynamical law for a quantum mechanical system with a finite number of levels is formulated. A fundamental role is played by the so-called "dynamical matrix" whose properties are stated in a sequence of theorems. A necessary and sufficient criterion for distinguishing dynamical matrices corresponding to a Hamiltonian time-dependence is formulated. The non-Hamiltonian case is discussed in detail and the application to paramagnetic relaxation is outlined.

I. INTRODUCTION

THE dynamical description of a mechanical system consists of three distinct aspects, namely (i) the choice of dynamical variables; (ii) the rule for assigning numerical values to the various functionals of the dynamical variables appropriate to the specification of the "state" of the system; and, finally (iii) the time dependence of this rule for assigning numerical values (equations of motion). The distinction between classical and quantum-mechanical systems is solely contained, in the second aspect; and it is well known that "related" classical and quantum-mechanical systems (i.e., those dealing with the same dynamical variables) have formally identical equations of motion.

In quantum mechanics it is conventional[1] to introduce the Schrödinger amplitude as a specification of the state; and the time-dependence of the state is expressed in terms of a time-dependent unitary transformation:

$$\psi(t)=U(t,t_0)\psi(t_0), \tag{1}$$

where $\psi(t)$ is the Schrödinger amplitude and

$$U(t,t_0)=\left(\exp\left\{-i\int_{t_0}^{t} H(t')dt'\right\}\right)_+ \tag{2}$$

is the time-ordered exponential of the time integral of the (Hermitian) Hamiltonian operator $H(t)$. (In the particular case of a constant Hamiltonian one may omit the time-ordering symbol, but this simplification is irrelevant to the present discussion.) The time dependence is here carried entirely by the "state" and is completely equivalent to the differential equations of motion in the "Schrödinger picture":

$$i[\partial\psi(t)/\partial t]=H(t)\psi(t). \tag{3}$$

An alternative form of the equations of motion is obtained by going to the "Heisenberg picture" in which the time dependence is carried entirely by the dynamical variables, the "state" being the same for all times:

$$\mathcal{O}(t)=U^\dagger(t,t_0)\mathcal{O}(t_0)U(t,t_0). \tag{4}$$

In either picture, the rule for assigning numerical values to the dynamical variable $\mathcal{O}$ is given by

$$\mathcal{O}\rightarrow\psi^\dagger\mathcal{O}\psi\equiv\langle\psi|\mathcal{O}|\psi\rangle. \tag{5}$$

While the dynamics is thus formulated in terms of the Schrödinger amplitude ψ, it is known that the general specification of the "state" of a quantum-mechanical system is somewhat more general[2] than is implied by Eq. (5); it corresponds to the choice of a Hermitian positive semidefinite matrix of unit trace and a rule for assigning numerical values to dynamical variables in the form:

$$\mathcal{O}\rightarrow\mathrm{Tr}\{\mathcal{O}\rho\}. \tag{6}$$

Since ρ is Hermitian, it can always be diagonalized in the form

$$\rho=\sum_r\lambda_r\psi_r\psi_r^\dagger=\sum_r\lambda_r|\psi_r\rangle\langle\psi_r|;\quad \sum_r\lambda_r=1, \tag{7}$$

where the non-negative numbers λ_r are the eigenvalues of the matrix ρ and ψ_r are the corresponding eigenvectors; hence one may rewrite the rule embodied in Eq. (6) in the form:

$$\mathcal{O}\rightarrow\sum_r\lambda_r\langle\psi_r|\mathcal{O}|\psi_r\rangle, \tag{8}$$

so that it is a weighted average of the values obtained by the rule Eq. (5) with the weight λ_r. In this manner one is led to consider the matrix as representing a suitable "ensemble" of kinematically identical systems and is called the "density matrix." But we prefer to ignore this "interpretation" and use the "state" of a *single* mechanical system to be completely specified by giving the

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[1] See, for example, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1958), 4th ed.

[2] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1955).

appropriate density matrix ρ. The "states" of a quantum-mechanical system (taken in this generalized sense) thus form a convex set of matrices and incoherent mixing of two states is simply given by a normalized linear combination. To a special class of density matrices correspond Schrödinger amplitudes, namely to those with all λ_r zero except one which is unity; for this special case the matrix ρ satisfies the equation

$$\rho^2=\rho. \tag{9}$$

(A coherent superposition of such states would again correspond to a matrix of the same type, but this matrix is not simply the normalized linear combination of the matrices.)

A natural assignment of the time dependence of these states is obtained from the decomposition according to Eq. (7) requiring the constants λ_r to be time independent but ψ_r to change with time in the manner given by Eq. (3). This Schrödinger picture equations are summarized by the law

$$\rho(t)=U(t,t_0)\rho(t_0)U^\dagger(t,t_0). \tag{10}$$

Completely equivalent to these are the Heisenberg picture equations in which the state is time independent but the dynamical variables change according to Eq. (4). In either case the matrix $U(t,t_0)$ is unitary and the time dependence is completely described by this unitary matrix or, equivalently, by the Hermitian Hamiltonian matrix $H(t)$.

However it is quite obvious that this dynamical law, though natural, is not the most general nor fully adequate; thus in treating problems of irreversibility and relaxation one has to deal with temporal changes of the density matrix which are not unitary and cannot thus be encompassed within a Hamiltonian scheme. The problem thus arises of developing a more general dynamical framework to deal with the time dependence of a general quantum-mechanical system, including the Hamiltonian scheme as a special case. It is to the formulation and solution of this problem that this paper is devoted.

The underlying ideas of this investigation are applicable to dynamical systems in general, both classical and quantum mechanical. However for reasons of simplicity of treatment and the immediate applicability to paramagnetic relaxation phenomena we have found it convenient to confine our attention to quantum-mechanical systems with a finite number of states. All the operators one has to deal with thus become finite-dimensional matrices. The theory so developed has points of similarity with the theory of Markov chains, but there are essential points of difference since the n-level system in quantum mechanics is described in terms of an $n\times n$ matrix rather than by a probability vector with n elements.

This paper, then, deals with stochastic processes in quantum-mechanical systems with a finite number of states, i.e., one which is associated with dynamical variables and states specified by finite-dimensional matrices. In Sec. 2 we deal with the general formulation of the problem; and Sec. 3 with the development of a necessary and sufficient condition for a dynamical law to be a Hamiltonian scheme. In Sec. 4 several auxiliary theorems are stated and proved and a canonical form of the "dynamical matrix" is presented. Several special cases of the dynamical matrices are enumerated in Sec. 5 and the case of paramagnetic relaxation in a strong magnetic field is studied. The final section includes a discussion of the relevance of this theory to questions of irreversibility in more complicated dynamical systems.

II. FORMULATION OF STOCHASTIC DYNAMICS

The kinematic restrictions on the density matrix ρ of an n-level system are the following[2]:

$$(\rho_{r,s})^*=\rho_{s,r}, \quad \text{(Hermiticity)} \tag{11}$$

$$x_r^*\rho_{r,s}x_s\geqslant 0, \quad \text{(positive semidefiniteness)} \tag{12}$$

$$\rho_{r,r}=1. \quad \text{(normalization)} \tag{13}$$

In the above we have invoked the summation convention, the indices running over the values

$$r,\, s=1,\, 2,\, \cdots,\, n.$$

The most general dynamical law relates a density matrix $\rho(t_0)$ with another density matrix $\rho(t)$ in a manner which depends on the two times t and t_0. If we require that the incoherent superpositions of two states $\rho^{(1)}(t_0)$ and $\rho^{(2)}(t_0)$ should correspond to the incoherent superpositions of $\rho^{(1)}(t)$ and $\rho^{(2)}(t)$ with the *same* normalized weights the most general dynamical law is given by the linear, homogeneous mapping:

$$\rho_{r,s}(t_0)\rightarrow\rho_{r,s}(t)=A_{rs,r's'}(t,t_0)\rho_{r's'}(t_0), \tag{14}$$

where $A_{rs,r's'}(t,t_0)$ is a numerical $n^2\times n^2$ matrix labelled by pairs of indices (rs) and $(r's')$ depending on the times t and t_0 but *independent* of the matrix $\rho(t_0)$. Since the linearity is demanded only for *normalized* incoherent superpositions,

$$\rho(t_0)=x\rho^{(1)}(t_0)+(1-x)\rho^{(2)}(t_0) \tag{15}$$

(with $0\leqslant x\leqslant 1$), it might appear that the general mapping is an inhomogeneous one of the form

$$\rho_{r,s}(t_0)\rightarrow\rho_{r,s}(t)=A_{rs,r's'}{}'(t,t_0)\rho_{r's'}(t_0)+a_{rs}(t,t_0), \tag{16}$$

with $a_{rs}(t,t_0)$ independent of $\rho_{r,s}(t_0)$. But one verifies immediately that (16) can be rewritten in the form (14) with

$$A_{rs,r's'}=A_{rs,r's'}{}'+a_{r,s}\delta_{r's'} \tag{17}$$

making use of (13).

Let us now discuss the restrictions imposed on the matrix $A_{rs,r's'}$. The consequences of (11), (12), (13) are,

respectively,

$$A_{sr,s'r'}=(A_{rs,r's'})^*, \tag{11'}$$

$$x_r^*x_sA_{rs,r's'}y_{r'}y_{s'}^*\geqslant 0, \tag{12'}$$

$$A_{rr,r's'}=\delta_{r's'} \tag{13'}$$

which give fairly complicated properties for the A matrix. To display these properties in a more transparent fashion, as well as for further development, it is advantageous to introduce another $n^2\times n^2$ matrix B related to A and defined by

$$B_{rr',ss'}=A_{rs,r's'}. \tag{14}$$

It immediately follows that B is Hermitian and positive semidefinite; we can rewrite (11′) and (12′) in the form:

$$B_{rr',ss'}=(B_{ss',rr'})^*,\quad \text{(Hermiticity)} \tag{15}$$

$$z_{rr'}^*B_{rr',ss'}z_{ss'}\geqslant 0.\quad \text{(positive semidefiniteness)} \tag{16}$$

The trace condition (13′) is still complicated and becomes

$$B_{rr',rs'}=\delta_{r's'}; \tag{17}$$

by summing with respect to the other indices also, we obtain the weaker statement

$$B_{rr',rr'}=\delta_{r'r'}=n. \tag{18}$$

Let us now consider the effect of a time-dependent change of basis on the matrix B. Under a change of basis generated by the unitary matrix $\alpha(t)$ at the final time, $\rho(t_0)$ is unaffected but $\rho(t)$ changes according to

$$\rho(t)\rightarrow\alpha(t)\rho(t)\alpha^\dagger(t), \tag{19}$$

or, equivalently,

$$\rho_{r,s}(t)\rightarrow\alpha_{\gamma,p}(t)(\alpha_{s,q})^*\rho_{p,q}(t).$$

Hence the transformation of the matrix B under the change of basis is given by

$$B_{rr',ss'}(t,t_0)\rightarrow\alpha_{r,p}(t)(\alpha_{s,q}(t))^*B_{pr',qs'}(t,t_0),$$

which may be written in the form

$$B\rightarrow\beta B\beta^\dagger, \tag{20}$$

where

$$\beta_{rr',ss'}=\alpha_{rs}\delta_{r's'} \tag{20'}$$

is a unitary matrix. Thus B undergoes a unitary transformation under a change of basis. In the particular case of a unitary time development according to (10), we can, by a suitable time-dependent change of basis make the density matrix time independent (Heisenberg picture) so that the B matrix assumes the simple form

$$B_{rr',ss'}=\delta_{rr'}\delta_{ss'}. \tag{21}$$

We thus see that the matrix B incorporates the kinematical restrictions on the dynamical law in a succinct fashion; we shall call B the "dynamical matrix." The results of this section can be summarized in the form of the following theorem:

Theorem 1. The dynamical matrix is a positive semidefinite $n^2\times n^2$ matrix with trace n and obeying the stronger partial trace relation given by (17). The dynamical matrices for different time-dependent choices of basis are unitarily related.

III. HAMILTONIAN DYNAMICAL MATRICES

Let us consider the unitary case in detail. From the special form (17) it follows that

$$(B^2)_{rr',ss'}=nB_{rr',ss'}.$$

In view of the unitary equivalence (20) of the B matrices for arbitrary choice of basis this relation is general; one thus has the characteristic equation for the dynamical matrix for unitary time dependence,

$$B^2-nB=0. \tag{22}$$

Hence the eigenvalues of B are n or 0 and, in view of the trace condition (18), the eigenvalue n is nondegenerate. The characteristic equation (22) could also be obtained from the general form,

$$B_{rr',ss'}=U_{rr'}(U_{ss'})^*, \tag{23}$$

for the dynamical matrix in the case of a unitary time dependence governed by the unitary matrix (10). Of course, by a proper choice of basis the dynamical matrix in this case can be brought to the standard form (21).

It is interesting to show that the converse also holds; more precisely, if B is a dynamical matrix satisfying the conditions stated in Theorem 1 as well as the characteristic equation (22) it corresponds to a unitary time dependence (10) if the density matrix and the dynamical matrix can be reduced to the form (23). To demonstrate this result we proceed as follows: let D be the matrix which diagonalizes B; since B is Hermitian, D can be chosen unitary[3] so that

$$D_{rr',tt'}(D_{ss',tt'})^*=\delta_{rr'}\delta_{ss'}. \tag{24}$$

By a proper choice of D it is possible to bring B to a diagonal form $\bar{B}$ with the eigenvalue n in the first place and zeroes elsewhere. But by definition

$$B=D^\dagger\bar{B}D,$$

so that

$$B_{rr',ss'}=n(D_{11,rr'})^*D_{11,ss'}. \tag{25}$$

We now invoke the trace condition (17) in the form

$$n(D_{11,rr'})^*D_{11,rs'}=\delta_{r's'}, \tag{26}$$

so that the $n\times n$ matrix

$$V_{rr'}=(n)^{\frac{1}{2}}(D_{11,rr'})^* \tag{27}$$

is unitary; the demonstration is complete if we notice

[3] See, for example, F. D. Murnaghan, *The Theory of Group Representations* (The Johns Hopkins Press, Baltimore, Maryland, 1938).

that (25) can be rewritten in the form

$$B_{rr',ss'}=V_{rr'}(V_{ss'})^*,$$

which is to be compared with (23). We have thus proved the following theorem:

Theorem 2. The necessary and sufficient condition for a dynamical matrix (satisfying the conditions of Theorem 1) to represent a Hamiltonian dynamics is that the dynamical matrix should satisfy the characteristic equation (22).

IV. NON-HAMILTONIAN DYNAMICAL MATRICES

In the general case one has no Hamiltonian and Eq. (22) would not be valid; in view of (16) the characteristic equation should imply non-negative eigenvalues and should be at most of degree n^2. Comparing the expression (23) for the dynamical matrix for unitary time dependence, the question then naturally suggests itself whether the general dynamical matrix is factorizable in the form

$$B_{rr',ss'}=X_{rr'}(Y_{ss'})^*, \tag{28}$$

with $X\neq Y$ in general. If this were true, from the Hermiticity of B it follows that

$$(X_{rr'})(Y_{ss'})^*=(X_{ss'})^*(Y_{rr'}),$$

so that

$$X_{rr'}/Y_{rr'}=(X_{ss'}/Y_{ss'})^*=1/c,$$

where c is a real constant independent of r, r', s, s' so that we have

$$Y_{rr'}=cX_{rr'}.$$

Substituting this expression into (28) and invoking the trace condition (17) it follows that

$$cX_{rr'}(X_{rs'})^*=\delta_{r's'},$$

so that $(c)^{\frac{1}{2}}X$ is a unitary matrix and we recover the unitary scheme (23). Thus we have the following theorem:

Theorem 3. Except in the case of unitary time dependence of the density matrix, the dynamical matrix cannot be factorized in the form (28).

We shall now present a canonical form for dynamical matrices in the general case using a generalization of the techniques employed in Sec. 3. Let us again consider the diagonalizing unitary $n^2\times n^2$ matrix D; in the general case consider the $n\times n$ matrices $W(q,q')$ defined by

$$W_{rr'}(qq')=D_{rr',qq'}. \tag{29}$$

Let $\mu(qq')$ be the n^2 non-negative eigenvalues (not necessarily distinct) of the dynamical matrix B which satisfy the trace condition:

$$\sum_{qq'}\mu(qq')=n. \tag{30}$$

The unitarity restriction (24) on D may be rewritten in terms of the matrices in the forms

$$\begin{gathered}\sum W_{rr'}(qq')(W_{ss'}(qq'))^*=\delta_{rr'}\delta_{ss'},\\ \mathrm{Tr}\{W^\dagger(qq')W(pp')\}=\delta_{pq}\delta_{p'q'}.\end{gathered} \tag{31}$$

The definition of the diagonalizing matrix D can now be rewritten in terms of the matrices $W(qq')$ to furnish a canonical form for the dynamical matrix:

$$B_{rr',ss'}=\sum_{q,q'}\mu(qq')W_{rr'}(qq')(W_{ss'}(qq'))^*. \tag{32}$$

The strong trace relation (17) ensures that the relation

$$\sum\mu(qq')W_{rs}(qq')W_{sr'}{}^\dagger(qq')=\delta_{rr'}, \tag{33}$$

will be valid. These results are stated in the following theorem:

Theorem 4. A general dynamical matrix can be written in the canonical form (32) in terms of n^2 matrices $W(qq')$ which obey the bilinear relations (31) and (33).

Note that the matrices $W(qq')$ are not necessarily unitary, but satisfy only the weaker condition (33). In the special case of a single nondegenerate nonzero eigenvalue for the dynamical matrix (33) reduces to the demonstration in Sec. 3 that $n^{\frac{1}{2}}W(11)$ is unitary. We shall see below that W matrices not proportional to unitary matrices have to be used for physically interesting relaxating systems.

Since density matrices form a homogeneous convex set one verifies that if

$$\rho_{rs}(t_0)\longrightarrow\rho_{rs}{}^{(i)}(t)=B_{rr',ss'}{}^{(i)}(t,t_0)\rho_{r's'}(t_0)$$

form a set of admissible dynamical laws, the mapping associated with the dynamical matrix,

$$B_{rr',ss'}=\sum\lambda_iB_{rr',ss'}{}^{(i)},\quad\sum\lambda_i=1,\quad\lambda_i\geqslant0$$

is also admissible. We have thus the theorem:

Theorem 5. Dynamical matrices form a homogeneous convex set.

V. SPECIAL DYNAMICAL MATRICES

We may now enumerate several special cases of dynamical matrices, exploiting in particular Theorem 5. Two simple sets of dynamical matrices are the following:

(i) Normalized linear combinations of "pure" matrices of the type (23) with different U matrices. This set may be identified with the representative of an ensemble in the sense that the dynamical law corresponds to an incoherent "mixture of dynamics" with different Hamiltonians.

(ii) "Relaxation generators" of the form:

$$B_{rr',ss'}=\sigma_{rs}\delta_{r's'}, \tag{34}$$

where σ_{rs} is any admissible density matrix; this corresponds to the mapping of every density matrix into the density matrix σ_{rs}. Note that B obeys the same characteristic equation as σ. While this mapping is itself unphysical, the convex set formed out of this set with the

last set corresponds to a standard relaxation phenomenon. Thus, for example, the matrix

$$B_{rr',ss'}=(1-\lambda)\delta_{rr'}\delta_{ss'}+\lambda\sigma_{rs}\delta_{r's'} \tag{35}$$

for $0<\lambda<1$ corresponds to a pure relaxation process with associated characteristic time $(t-t_0)/\lambda$.

The relaxation considered here is a very simple kind of relaxation namely, one which is governed by a simple relaxation time and this may be seen to be an immediate consequence of the fact that the factor $\delta_{r's'}$ yields unity when applied to *any* density matrix. If we construct the more general "relaxation generators"

$$b_{rr',ss'}=\sigma_{rs}\tau_{r's'}, \tag{36}$$

or the more general form

$$b_{rr',ss'}=\sum_\alpha \sigma_{rs}{}^{(\alpha)}\tau_{r's'}{}^{(\alpha)} \tag{36'}$$

(where τ is an admissible density matrix), they may be used to describe more complex relaxation processes in terms of dynamical matrices formed in the manner of (36).

To make these statements more specific, let us consider the special case of paramagnetic relaxation in a strong external magnetic field[4]; and to simplify matters let us neglect all multipole polarizations except the magnetic dipole moment. Let us choose a basis which "transforms away" the unitary time dependence. We are then left with a dipole polarization which undergoes pure relaxation, the transverse and longitudinal parts relaxing at different rates. Let us choose the z axis to be in the direction of the external magnetic field. Consider the dynamical matrix

$$B_{rr',ss'}=(1-\lambda)\delta_{rr'}\delta_{ss'}+\lambda\sigma_{rs}\delta_{r's'} +\mu\left(\sigma_{rs}-\frac{1}{n}\delta_{rs}\right)\left(\sigma_{r's'}-\frac{1}{n}\delta_{r's'}\right), \tag{37}$$

where λ $(0<\lambda<1)$ and μ are suitable parameters; we can easily verify that this matrix is an admissible dynamical matrix and describes relaxation of an arbitrary density matrix towards σ. The ratio of longitudinal and transverse relaxation times is given by

$$\tau^{\text{long}}/\tau^{\text{tr}}=\lambda\bigg/\left\{\lambda-\mu\left(\text{Tr}(\sigma^2)-\frac{1}{n}\right)\right\}. \tag{38}$$

[4] F. Bloch, Phys. Rev. **70**, 460 (1946).

The method of construction can be generalized to accommodate arbitrary multipole polarizations.

One verifies that this class of dynamical matrices have the canonical form (32), but they cannot be obtained as the weighted average of "pure" matrices of the type, since all such matrices map the matrix

$$\rho_{r's'}(t_0)=(1/n)\delta_{r's'}$$

into itself and are thus unable to accommodate relaxation towards the steady state σ. In conclusion we may also point out that in the case of paramagnetic relaxation the relaxation mechanism has the same symmetry as the external polarizing field and hence the relaxation generators are invariant under the change of basis implicit in the "transforming away" of the unitary time dependence.

VI. DISCUSSION

In the previous sections we have discussed what may be called "forms of stochastic dynamics" in quantum-mechanical systems. While the discussion was confined to systems associated with $n\times n$ matrices the notions of mapping of density matrices, convex sets and canonical forms are relevant to the general case. With the more general notion of a state as a "rule for assigning numerical values to dynamical variables" is naturally associated a more general dynamical framework and the non-Hamiltonian nature of this more general framework is the major outcome of this investigation. Such non-Hamiltonian dynamical frameworks are known in classical field theory, but they are rarely treated from the present point of view. To mention two familiar instances (generally handled by entirely different and special methods), we may mention the decay of turbulence[5] in hydrodynamics and the passage of partially coherent partially polarized light through a medium.[6] A systematic study of these topics from the present point of view will be discussed elsewhere.

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[5] See, for example, G. K. Batchelor, *The Theory of Homogeneous Turbulence* (Cambridge University Press, New York, 1956).

[6] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, New York, 1959).