

Stability of quantum motion in chaotic and regular systems

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The evolution of a quantum state is altered when a small perturbation is added to the Hamiltonian. As time progresses, the overlap of the perturbed and unperturbed states gives an indication of the stability of quantum motion. It is shown that if a quantum system has a classically chaotic analog, this overlap tends to a very small value, with small fluctuations. On the other hand, if the classical analog is regular, the overlap remains appreciable (on a time average) and its fluctuations are much larger.

I. INTRODUCTION

The motivation of this work is to try to understand irreversibility in quantum theory. As explained in Sec. II, the standard explanation of irreversibility in classical physics (namely, mixing and coarse graining) cannot be carried over to quantum theory. An alternative explanation is proposed, based on the instability of Hamiltonian orbits with respect to small external perturbations. This explanation can readily be reformulated in quantum language.

Section III gives explicit formulas showing how the evolution of a quantum state deviates from its original Hamiltonian orbit if a small perturbation is added to the Hamiltonian. The overlap of the perturbed and unperturbed states gives an indication of the stability of quantum motion. It is argued that if a quantum system has a classically chaotic analog, this overlap must tend to a very small value, with small fluctuations. On the other hand, if the classical analog is regular, the overlap remains appreciable (on a time average) and its fluctuations are much larger.

In Sec. IV some numerical calculations are presented, supporting the above (admittedly heuristic) claims. In Sec. V these results are generalized to situations where the initial state is not pure and must be represented by a density matrix. Finally, Sec. VI examines the implications of these results with respect to the notion of irreversibility.

II. IRREVERSIBILITY IN CLASSICAL AND QUANTUM PHYSICS

The intuitive meaning of “irreversibility” is that there are some dynamical evolutions which can easily be prepared, but it is extremely difficult (we say “impossible”) to prepare the time-reversed evolutions. For example, it is easy to get a cup of lukewarm water by placing, one hour earlier, a cube of ice in a cup of boiling water. It is impossible to prepare a cup of lukewarm water in such a way that, one hour later, it will turn into an ice cube floating in boiling water.

The familiar *classical* explanation of irreversibility is based on the notions of *mixing* and *coarse graining*. Mixing is a property of chaotic systems, which can be proved rigorously (under suitable assumptions).¹ It essentially

means the following: Consider two finite (and *fixed*) subsets of phase space, say V_1 and V_2 , whose measures are fractions μ_1 and μ_2 of the total phase space. Suppose that the distribution $f_1(p, q)$ is uniform in V_1 at time t_1 , with $\int f_1 dV_1 = 1$. Then, for any time t_2 *sufficiently remote* from t_1 (in the future *or* the past) and for sufficiently large μ_1 and μ_2 , we have $|\int f_2 dV_2 - \mu_2| < \delta$, with arbitrarily small δ , irrespective of where V_1 is. This is the property called mixing. Notice that it is *time symmetric*. By itself it cannot explain irreversibility. Notice also that the smaller δ or μ_1 or μ_2 , the larger the time $|t_1 - t_2|$ needed for mixing. (In the paper I consider only *finite* times, not the unattainable mathematical limit of infinite time.)

In the ice-cube paradigm we have μ_1 (ice cube plus boiling water) $\ll \mu_2$ (lukewarm water) $\simeq 1$. Therefore, with a suitable value of the total energy, *almost every* evolution will lead to a cup of lukewarm water, with only extremely small inhomogeneities. Nevertheless, we *can*, conceptually, prepare the lukewarm water at time t_2 so that, at a *later* time t_1 it will separate into an ice cube and boiling water. This “only” requires a very special preparation (not just any cup of lukewarm water, but one with delicate correlations between all the molecules) and this preparation has a μ_2 *so small* that the mixing property, as defined above, will not yet be valid after the given *finite* time $t_1 - t_2$.

Now comes *coarse graining*. We may be unable, because of the coarseness of our instruments, to achieve such a preparation. We cannot locate the initial state within such a small V_2 (i.e., with μ_2 so small that mixing has not yet occurred after a finite $t_1 - t_2$). In summary, we cannot prepare the system at time t_2 so that, after a finite time $t_1 - t_2$, it will be located with certainty in the desired small region V_1 of phase space. There are evolutions (e.g., from lukewarm water to an ice cube in boiling water) which cannot be made to proceed.

The above argument explains classical irreversibility, but it fails in quantum theory, because the Wigner distribution² in phase space has a much smoother evolution³ than the Liouville-Gibbs distribution. It cannot develop “whorls and tendrils”⁴ on scales smaller than \hbar . Therefore it does not lead to the mixing property, as defined above. Moreover, coarse graining seems to make no sense

in the quantum language or, in fact, any language where dynamical variables occur with *discrete* values. It is in principle possible to prepare arbitrary, pure quantum states.⁵ Even if there is a small error in the preparation of the initial state, this error will not grow, because the Hamiltonian evolution is *unitary*: The scalar product of any two states is invariant, therefore two initially neighboring states will always remain neighbors in Hilbert space.

How can we have irreversibility in the microworld, without coarse graining? To explain this I propose another mechanism causing irreversibility, which is valid in both classical and quantum physics. Instead of assuming that our preparations are marred by limited accuracy, we may assume that they are perfect but, on the other hand, the Hamiltonian H is not exactly known, because we cannot perfectly insulate the physical system from its environment. We may thus consider a *family of Hamiltonians*⁶

$$H(\epsilon) = H + \epsilon_1 V_1 + \cdots + \epsilon_n V_n, \quad (1)$$

where H describes the free (perfectly isolated) system, the V_k are any functions of its dynamical variables, and the ϵ_k (denoted collectively as ϵ) are small unknown parameters, possibly time dependent. For example, the behavior of a molecule which is not perfectly shielded from electromagnetic fields may be described by taking as ϵ_k various components of \vec{E} and \vec{B} , their gradients, etc., and then the V_k will be the corresponding multipole moments of the molecule.

We now assume that the ϵ_k have a probability distribution $p(\epsilon_1 \dots \epsilon_n)$. This is the assumption which replaces coarse graining and which is, after all, quite realistic. Thus, we may assume that we start from a given *point* in phase space but, as time evolves, this point diffuses into a small cloud (so that we effectively have a kind of coarse graining). The discussion then proceeds as before. After a finite time, ordinary mixing, due to H , ensures that the cloud has diffused uniformly throughout the entire accessible phase space (i.e., all the regions which are not forbidden by the conservation laws of H).

Here it is important to distinguish regular from chaotic Hamiltonians.^{7,8} A regular Hamiltonian, e.g., one having as many constants of motion in involution as there are degrees of freedom, does not lead to mixing because of the Kolmogorov-Arnol'd-Moser (KAM) theorem: Slightly perturbed orbits remain on neighboring tori and separate slowly. Their separation is typically linear in time. On the other hand, the orbits of a chaotic Hamiltonian explore the entire energy surface and their separation grows exponentially with time. This results in the mixing property discussed above.

The approach embodied in Eq. (1) can easily be transcribed in quantum language. Consider the simplest case where the ϵ_k are time independent. The initial density matrix ρ_0 evolves as

$$\rho_0 \rightarrow e^{-iH(\epsilon)t/\hbar} \rho_0 e^{iH(\epsilon)t/\hbar}. \quad (2)$$

Since the small parameters ϵ_k are unknown, one must take an average over their probability distribution. One

thereby obtains

$$\rho(t) = \int e^{-iH(\epsilon)t/\hbar} \rho_0 e^{iH(\epsilon)t/\hbar} p(\epsilon) d^n \epsilon. \quad (3)$$

Even if ρ_0 is a pure state ($\rho_0^2 = \rho_0$), $\rho(t)$ will be a mixture. Its entropy $-\text{Tr}(\rho \ln \rho)$ is positive. The remainder of this paper is devoted to some quantitative estimates.

III. STABILITY OF QUANTUM EVOLUTION

I shall henceforth consider, for the sake of simplicity, a Hamiltonian

$$H' = H + \epsilon V, \quad (4)$$

where H and V are *known*. Moreover, the parameter ϵ (also known) is assumed constant and so small that time-independent perturbation theory is valid: The eigenvalues and eigenvectors of H' are very close to those of H and can be obtained from them by standard formulas.

A physical system is prepared in an initial state ϕ and the problem is to compare its evolution $e^{-iH't/\hbar} \phi$ with the unperturbed evolution $e^{-iHt/\hbar} \phi$, for large t . The intuitive expectation (supported by the calculations below) is that the overlap

$$S(t) = |(e^{-iHt/\hbar} \phi, e^{-iH't/\hbar} \phi)|^2 \quad (5)$$

will decay to a much lower value if H is chaotic than if it is regular. Not only the time average of $S(t)$, denoted by \bar{S} , but also the rms fluctuations around \bar{S} ought to be much smaller for a chaotic system than for a comparable regular one.

Here the reader may object that it is difficult to produce an unbiased comparison between different physical systems (such as a regular one and a chaotic one). However, there are some classical Hamiltonians having both regular and chaotic orbits, in different regions of phase space.^{9,10} The quantized versions of these Hamiltonians then have "regular states" and "chaotic states," which are well separated¹¹ in the semiclassical limit $\hbar \rightarrow 0$. It is therefore meaningful (and unbiased) to compare the relative stabilities of different states of the *same* system.

To compute (5) explicitly, we expand ϕ into the eigenfunctions of H and H' :

$$\phi = \sum_m a_m u_m = \sum_m a'_m u'_m, \quad (6)$$

where

$$H u_m = E_m u_m, \quad (7)$$

and

$$H' u'_m = E'_m u'_m. \quad (8)$$

Here we have assumed that the same set of quantum numbers (denoted collectively as m) can be used to label the eigenvectors of H and those of H' . For a regular Hamiltonian, these quantum numbers may refer to a complete set of commuting observables, including H . For a chaotic Hamiltonian, there are no such quantum numbers¹² but, on the other hand, there is a tendency to level repulsion^{11,13} so that, for small enough ϵ , it is still possible to identify corresponding levels.¹⁴

In any case, we have, from time-independent perturba-

tion theory,

$$E'_m = E_m + V_m, \quad (9)$$

where

$$V_m = (u_m, V u_m). \quad (10)$$

Moreover,

$$(u_m, u'_n) \simeq \delta_{mn} \quad (11)$$

and $a'_m \simeq a_m$, to order ϵ . It follows that

$$S(t) = \left| \sum_m c_m \exp(-iV_m \tau) \right|^2, \quad (12)$$

where

$$c_m = |a_m|^2 \quad (13)$$

and

$$\tau = \epsilon t / \hbar. \quad (14)$$

These formulas hold for small enough ϵ . In fact, the only place where ϵ cannot be neglected is in τ , because t may be large.

The behavior of (12) is very different in systems having regular and chaotic Hamiltonians, for usual preparations of these systems. Indeed, assume that the initial state ϕ is prepared by selecting systems having a given eigenvalue of a "reasonable" operator^{15,16} (such as a polynomial in the canonical variables p and q). Then, for a regular system, the a_m satisfy selection rules.^{12,17} Most of them vanish (or are very small) and only a few are large (an example is given in Sec. IV). It follows that $S(t)$ must oscillate with a fairly large amplitude. Its time average (assuming no degeneracy) is

$$\bar{S} = \sum_m c_m^2, \quad (15)$$

which is dominated by the few largest c_m . [Strictly speaking, $S(t)$ is almost periodic, but the recurrence time may be inordinately long,¹⁸ unless *very* few a_m are involved.]

On the other hand, if H is chaotic, a reasonable ϕ has many small a_m , randomly distributed.^{12,17} Therefore \bar{S} is small (typically, it is of the order of $1/N$, where N is the number of energy levels appreciably represented in ϕ). For the same reason, the rms fluctuations $\overline{S^2} - \bar{S}^2$ are small.

All the foregoing deals with the behavior of $S(t)$ for large (but finite) t . On the other hand, there is no reason whatsoever that the *initial* decay rate of $S(t)$ should be larger for chaotic than for regular systems. It is in fact completely independent of the Hamiltonian. Indeed, if we expand $S(t)$ in a power series for small t , we obtain

$$S(t) = 1 - (\Delta V)^2 \tau^2 + \dots, \quad (16)$$

where

$$(\Delta V)^2 = \sum_m c_m^2 V_m^2 - \left[\sum_m c_m V_m \right]^2, \quad (17)$$

$$= (\phi, V^2 \phi) - (\phi, V \phi)^2. \quad (18)$$

This only depends on the perturbation V and the initial state ϕ (not on H). It can in fact be rigorously proved that¹⁹

$$S(t) \geq \cos^2(\Delta V \tau) \quad (19)$$

for $\Delta V \tau < \pi/2$.

For large t , the behavior of $S(t)$ depends on the statistical properties of the V_m . We write

$$S(t) = \sum_{m,n} c_m c_n \cos(V_m - V_n) \tau, \quad (20)$$

$$= \bar{S} + \sum'_{m,n} c_m c_n \cos(V_m - V_n) \tau, \quad (21)$$

where we have used (15) and where the summation $\sum'_{m,n}$ excludes terms with $m=n$. We further assume that the c_m are statistically independent of the V_m . Taking an ensemble average (e.g., over many different types of perturbation and initial states), we obtain

$$\langle S(t) \rangle = \langle \bar{S} \rangle + \left\langle \sum'_{m,n} c_m c_n \right\rangle \langle \cos(V_m - V_n) \tau \rangle. \quad (22)$$

Now, by virtue of (15)

$$\sum'_{m,n} c_m c_n = \sum_{m,n} c_m c_n - \bar{S} = 1 - \bar{S}, \quad (23)$$

since $\sum_m c_m = 1$. It follows that

$$\langle S(t) \rangle = \langle \bar{S} \rangle + (1 - \langle \bar{S} \rangle) \langle \cos(V_m - V_n) \tau \rangle. \quad (24)$$

The decay law of $\langle S(t) \rangle$ thus depends on the statistical distribution of $|V_m - V_n|$.⁶ For example, if the latter is Gaussian, the behavior of $\langle S(t) \rangle$ is Gaussian too.

IV. NUMERICAL SIMULATIONS

To test the above conjectures, I used the coupled rotator model with Hamiltonian^{10,20}

$$H = L_z + M_z + L_x M_x. \quad (25)$$

Here, \vec{L} and \vec{M} are two independent angular momenta. The constants of motion of this system are H , L^2 , and M^2 . For some values of these constants the *classical* system with Hamiltonian (25) is regular, and for other values it is chaotic.¹⁰ These properties are reflected in its quantum-mechanical spectrum^{13,21} and matrix elements.²⁰

For given values of the constants $L^2 = \hbar^2 l(l+1)$ and $M^2 = \hbar^2 m(m+1)$, the Hamiltonian (25) is a *finite* matrix of order $(2l+1)(2m+1)$. I have taken, as in Ref. 20, $l=m=20$ and $\hbar=0.1707825$. This corresponds to $L=M=3.5$. The energy eigenstates of this system appear to be mostly regular if $|E| \gtrsim 9$ and mostly chaotic if $|E| \lesssim 6$. This is what was found in the *static* calculations.^{20,21} I shall now investigate differences in the *dynamical* behavior of *nonstationary* quantum states.

It is convenient to label a basis in Hilbert space (for given $l=m$) by

$$j_z = l_z + m_z \quad (26)$$

and

$$k_z = l_z - m_z. \quad (27)$$

TABLE I. Statistical properties of the two initial states.

Initial state	$\langle H \rangle$	ΔH	$\langle V \rangle$	ΔV	\bar{S}
$ 40,0\rangle$	6.8313	0.2917	3.2950	0.7386	0.1968
$ 0,0\rangle$	0	0.6125	0	4.5115	0.0069

The Hilbert space then splits into four disjoint subspaces, with j_z even or odd, and $|j_z, k_z\rangle = \pm |j_z, -k_z\rangle$. The Hamiltonian (25) has no matrix elements connecting these subspaces. It is therefore convenient to consider just one of them, for example, the even-even subspace, having dimension $21^2 = 441$.

As the perturbation V in Eq. (4) I took

$$V = L_x M_x, \quad (28)$$

which, like H , has no matrix elements connecting the four invariant subspaces. I considered two initial states, $|40,0\rangle$ and $|0,0\rangle$, which were expected to behave regularly and chaotically, because the corresponding values of $\langle H \rangle$ are in the regular and chaotic regions, respectively (see Table I).

Moreover, as shown in Table II, the $|40,0\rangle$ state has an energy dominated by a few, strong, nearly equidistant lines. On the other hand, the $|0,0\rangle$ state has numerous weak lines of roughly the same magnitude. Note that these two sets of lines belong to the *same* energy spectrum. The regular or chaotic nature of the states is not a property of the energy spectrum alone, but is controlled by *how the most populated levels are related*. Those of $|40,0\rangle$ are nearly equidistant (they are all within 0.2% of $E = 6.794 + 0.213n$, with $n = 0, \pm 1$) as expected from the correspondence principle, for classically periodic motion.^{13,22} Those of $|0,0\rangle$ do not show any such regularity.

The behavior of $S(t)$ is shown in Fig. 1. As expected, the time average $\bar{S} = \sum_m c_m^2$ is considerably smaller for the chaotic initial state $|0,0\rangle$ than for the regular one $|40,0\rangle$.

The physical meaning of $S(t)$ is the probability to get an affirmative answer to the question, "Is the final state of the system $e^{-iHt/\hbar}\phi$?" or, in other words, "Is the final state unaffected by the perturbation?" (Notice that it is experimentally meaningless to ask, "What is the state of a

TABLE II. The most populated energy levels of the initial states.

$ 40,0\rangle$		$ 0,0\rangle$	
E_n	c_n	E_n	c_n
6.801 926	0.381 937 6	$\pm 1.074 954$	0.023 537 8
6.994 843	0.153 378 1	$\pm 11.056 02$	0.017 808 1
7.019 689	0.114 185 5	$\pm 11.575 16$	0.014 828 6
6.581 356	0.078 724 7	$\pm 2.298 508$	0.013 251 7
6.791 842	0.060 114 6	0	0.012 087 5

$$\sum_{n=1}^5 c_n = 0.788 340 5$$

$$\sum_{n=1}^9 c_n = 0.150 939 9$$

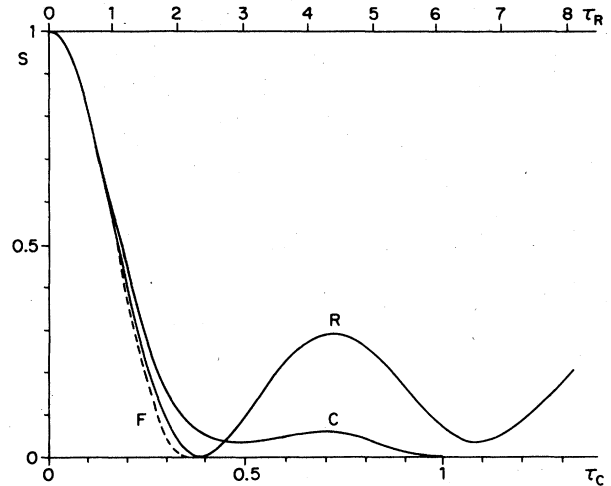


FIG. 1. The overlap function $S(t)$ for the initial states $|R\rangle = |40,0\rangle$ and $|C\rangle = |0,0\rangle$. The time axes are labeled by $\tau = \epsilon t/\hbar$ and drawn with units inversely proportional to ΔV , so that the initial decay rates appear the same. The dashed line F is Fleming's unitary limit (Ref. 19) $\cos^2(\Delta V \tau)$.

system?"^{23,24} We can only ask, "Is the system in some given state?" Thus, in the present case, the probability that $|R\rangle$ is unaffected by the perturbation is, on a time average, 19.68% (see Table I). The probability that $|C\rangle$ remains unaffected is only 0.69% (i.e., in 99.31% of cases, the evolution starting from $|C\rangle$ leads to a state which is orthogonal to $e^{-iHt/\hbar}|C\rangle$).

It is remarkable that the time average \bar{S} and the fluctuations around it are independent of the perturbation parameter ϵ (as long as the latter is small enough so that time-independent perturbation theory is valid). The value of ϵ affects only the time scale, as shown in Eq. (14).

V. DENSITY MATRICES

These results are readily generalized to the case where the initial preparation is not represented by a pure state but by a density matrix ρ . Instead of (5) we have

$$S(t) = \text{Tr}(e^{-iHt/\hbar} \rho e^{iHt/\hbar} e^{-iH't/\hbar} \rho e^{iH't/\hbar}) / \text{Tr}(\rho^2). \quad (29)$$

It is easily seen that this reduces to (5) in the pure-state case, where $\rho = P_\phi$ is the projection on state ϕ . The opposite extreme is a perfect mixture ($\rho = I/N$, where N is the dimensionality of Hilbert space), for which one has $S(t) = 1$, trivially.

In the general case, it is convenient to write ρ in diagonal form

$$\rho = \sum_k w_k P_k, \quad (30)$$

where the P_k are projection operators on a set of orthogonal states v_k and the w_k are non-negative numbers whose sum is 1. We then have

$$\text{Tr}(\rho^2) = \sum_k (w_k)^2, \quad (31)$$

and

$$\text{Tr}(e^{-iHt/\hbar} \rho e^{iHt/\hbar} e^{-iH't/\hbar} \rho e^{iH't/\hbar}) = \sum_{j,k} w_j w_k S_{jk}(t), \quad (32)$$

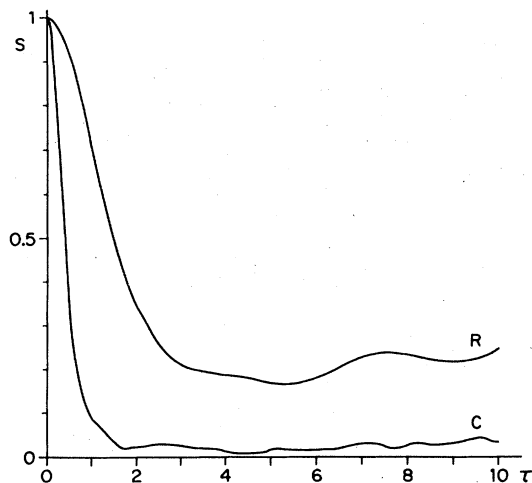


FIG. 2. The overlap function for two density matrices consisting of an equal weight mixture of six states in the regular region and in the chaotic region, respectively.

where

$$S_{jk}(t) = |(e^{-iHt/\hbar} v_j, e^{-iH't/\hbar} v_k)|^2. \quad (33)$$

All these quantities are readily calculated in any specific case. We write, as in (6),

$$v_k = \sum_m a_{km} u_m, \quad (34)$$

and obtain

$$S_{jk}(t) = \left| \sum_m a_{jm}^* a_{km} \exp(-iV_m \tau) \right|^2, \quad (35)$$

which generalizes Eq. (12). Finally,

$$S(t) = \sum_{j,k} w_j w_k S_{jk}(t) / \sum_n (w_n)^2. \quad (36)$$

As an example, using again Hamiltonian (25), I took two sets of six states: a "regular set" with $j_z \geq 36$ and a "chaotic set" with $-2 \leq j_z \leq 2$ and $k_z = 0, 2$. In both cases all the w_n were taken equal to $\frac{1}{6}$. The result is shown in Fig. 2. As expected from the averaging process, the resulting curves are much smoother (have smaller fluctuations) than in Fig. 1.

On a time average we have, from (35),

$$\bar{S}_{jk} = \sum_m |a_{jm}|^2 |a_{km}|^2. \quad (37)$$

In the chaotic case this is typically of the same order of magnitude as (15). As there are, in our example, 36 terms in the numerator of (36) and only 6 terms in the denominator, this explains why curve C in Fig. 2 is about six times higher than in Fig. 1.

On the other hand, in the regular case the existence of selection rules implies that most \bar{S}_{jk} are very small for $j \neq k$. This explains why curve R of Fig. 2 does not lie much higher than in Fig. 1.

VI. WHITHER IRREVERSIBILITY?

It is now possible to reformulate in quantum language the "ice cube and boiling water" paradigm. Suppose that

we want to prepare an initial state ϕ so that, a time t later, the state of the system will be, with a high probability, in some given subspace of Hilbert space. This subspace is spanned by a set of orthonormal vectors v_1, \dots, v_n , with corresponding projection operators P_1, \dots, P_n . Let

$$P = \sum_k P_k. \quad (38)$$

We thus want to have

$$(e^{-iHt/\hbar} \phi, P e^{-iHt/\hbar} \phi) \simeq 1, \quad (39)$$

or, more generally, for an initial density matrix ρ ,

$$\text{Tr}(e^{-iHt/\hbar} \rho e^{iHt/\hbar} P) \simeq 1. \quad (40)$$

Here the projection operator P is given and the problem is to find the initial ϕ or ρ . It is assumed that we have perfect control on the initial conditions, so that *any* initial state can be prepared.⁵

A possible solution of (39) is

$$\phi = e^{iHt/\hbar} \chi, \quad (41)$$

where χ is *any* vector in the assigned subspace, satisfying $P\chi = \chi$. More generally, we have

$$\rho = \sum_k w_k e^{iHt/\hbar} P_k e^{-iHt/\hbar}, \quad (42)$$

with arbitrary non-negative w_k , satisfying $\sum_k w_k = 1$.

The difficulty is that we have no perfect control on H , because no system can be perfectly isolated from its environment. Actually, the Hamiltonian is some perturbed H' , as in Eq. (4). The question thus is, how far will the small perturbation ϵV carry us away from the targeted subspace?

This is precisely the kind of question which was discussed in the preceding sections. It was shown that the evolution of a *regular* system was only moderately affected by an external perturbation. In the examples given, the right-hand sides of (39) and (40) were of order 0.2 or 0.3. In other words, there was an appreciable chance to hit the target, even after a very long time.

On the other hand, for *chaotic* systems, the right-hand side of (39) or (40) was very small, with small rms fluctuations. Thus, the chance to end up the evolution in a prescribed subspace of Hilbert space was virtually nil (unless that subspace was very big).

In real life, this difficulty is met, for example, in selective photochemistry.²⁵ Suppose that we want to break a certain bond in a large molecule—but not the weakest bond. In principle a laser beam could supply enough energy to that particular bond, leaving the other ones cold. It should then be possible to determine *a priori* the bond which is most likely going to break.²⁶ However, it is found experimentally that intramolecular energy transfer dissipates the laser energy very rapidly among the other bonds or the different vibrational states. Considerable theoretical efforts have been devoted to explain this phenomenon.^{27–32}

In the approach presented here, the inability to excite and break a given bond can be explained as follows. The "bond excitations" are not the true normal modes—the

energy eigenstates—of the entire molecule. In standard molecular-dynamics calculations an approximation is made whereby attention is focused on a few “relevant” degrees of freedom and all the other ones are ignored. The latter then play the role of the “environment,” simulated in the present work by an ϵV perturbation. Then, if the dynamics of the relevant degrees of freedom is chaotic, it is impossible to concentrate enough energy on a particular bond so as to break it selectively. This is so because the state (or density matrix) with only that bond highly excited is a tiny subspace of the Hilbert space, just as the ice cube in boiling water was located in a tiny fraction of the

classical phase space. In that situation, nearly every dynamical evolution must miss the mark.

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