On the foundation of equilibrium quantum statistical mechanics

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Abstract

We discuss the condition for the validity of equilibrium quantum statistical mechanics in the light of recent developments in the understanding of classical and quantum chaotic motion. In particular, the ergodicity parameter introduced in [1] is shown to provide the conditions under which quantum statistical distributions can be derived from the quantum dynamics of a classical ergodic Hamiltonian system.

DYSCO 80

October 1997

PACS number 05.30.-d
I. INTRODUCTION

The pioneering works of Fermi, Pasta, Ulam(FPU) and the mathematical results originating from the ideas of Kolmogorov (see, e.g., Refs. [3]) in the mid fifties, have started a new era in our understanding of the behaviour of dynamical systems. At their first appearance these results were considered by most physicists as merely an interesting curiosity with no real physical relevance. The dominant belief was that, though they were correct, the large number of degrees of freedom and the complexity of the interaction of physical systems would inevitably lead to the validity of traditional statistical laws. For example these results did not shake the great confidence in the postulate of \textit{“a priori equiprobability”} or the Boltzmann ergodic hypothesis. It was generally believed that there is nothing in the laws of mechanics which would lead to expect that an isolated system is more likely to be in one of its accessible states than in another. The validity of this view was supported by the agreement of theoretical predictions with experimental observations.

More recently, examples of dynamical systems have been found, for which the ergodic hypothesis has been rigorously shown to be valid [4]. In particular it has become clear that for the validity of statistical laws the so-called thermodynamic limit is not necessary. The property of mixing or positive KS entropy is sufficient to ensure good statistical behaviour provided the number of degrees of freedom \( N > 2 \). Thus, an isolated system, no matter what the initial condition may be, will indeed reach a final equilibrium situation in which it is equally likely to be found in any one of its accessible states. In terms of distribution functions one may consider an ensemble of systems which are initially in some subset of the accessible states. During time evolution these systems will make transitions between the various accessible states until they are uniformly distributed and this will correspond to the final equilibrium situation. In this connection we would like to recall that the process of statistical relaxation is obviously time-reversible but the evolution of the distribution function is non recurrent.

Once the above mixing property has been assumed or shown to hold, then statistical
averages of physical quantities can be performed via the microcanonical or the equivalent canonical ensemble. To be more specific, let us consider a conservative, Hamiltonian system with \( N \) degrees of freedom:

\[
H = H_0 + V
\]  

(1.1)

where \( H_0 \) is some integrable Hamiltonian, for example a system of \( N \) independent harmonic oscillators, and \( V \) a non integrable perturbation. If the perturbation \( V \) is such that it renders the hamiltonian (1.1) ergodic and mixing, then, for any initial state, the system will approach a microcanonical equilibrium. As a consequence, the equipartition theorem can be rigorously proven, which means that, for example, for sufficiently small \( V \) there is energy equipartition among the different oscillators. Analogously, since the microcanonical ensemble implies equal probability for equal regions of the energy surface, it follows that the most probable distribution of particles among their own individual states for a system in macroscopic equilibrium is given by the Maxwell Boltzmann law \(^{[6]}\): namely, the probability that a particle has energy \( \epsilon \) is proportional to \( \exp(-\alpha \epsilon) \).

On the other hand it is now known that, if the perturbation is small enough then, generically, invariant regions of positive measure exist on the energy surface, most orbits lie on \( N \)-dimensional tori and typically the motion is ergodic over these tori only (and not on the \( 2N-1 \) dimensional energy surface). Therefore, the microcanonical ensemble cannot be used to compute statistical averages and the equipartition theorem does not hold: different regions on the energy surface are not equally probable and the average equilibrium values strongly depend on the initial conditions.

Certainly, the problem remains open to establish, for any given system, whether it is ergodic or not, with positive KS entropy or not etc. In other words, it is not practically known, rigorously speaking, when one can in fact be sure of the validity of the microcanonical ensemble. (We know from the Siegel theorem \(^{[5]}\) that in the space of Hamiltonian systems the vast majority of them is non integrable.) Actually, an entire new field, chaos and dynamical systems, has arisen from this problem. Nevertheless, at present, as far as the foundation of
II. THE QUANTUM ERGODIC PROBLEM

The problem now is what happens in quantum mechanics, which is the subject of the present paper. Existing standard textbooks assume the validity of the microcanonical (and canonical) ensemble and then proceed to derive, in several different ways, Bose-Einstein or Fermi-Dirac statistics, depending on the symmetry requirements. The idea behind this is to devise a representative ensemble of systems and then take the average properties of the systems in this ensemble as good estimates for quantities pertaining to the system of actual interest. The representative ensemble is constructed according to the postulate of a priori probability which is considered as a non arbitrary postulate. According to existing standard textbooks on the subject \[6\] "... it is also evident that it would be arbitrary to proceed otherwise than by assignment of random phases, since the quantum mechanics has not itself provided any reason for thinking that any particular arrangement of phases is inherently more probable than a random one... We now see that our postulate, of equal a priori probabilities and random a priori phases for different quantum mechanical states, is equivalent at the correspondence principle limit to the assumption of equal a priori probabilities for different regions of equal extension \(h^I\) in the classical phase space ... the postulate actually introduced is the only non arbitrary one that can be selected, and agrees at the correspondence principle limit with that selected for the classical statistic. The methods developed do have, as far as is known, the a posteriori justification of agreement with experimental findings". Quite clearly, this point of view has no solid theroretical grounds and indeed, as remarked in \[7\], "... such a point of view is not entirely satisfactory because these postulates cannot be independent of, and should be derivable from, the quantum mechanics of molecular systems. A rigorous derivation is at present lacking"

At a more rigorous level, the problem of quantum ergodicity was discussed for the first time in a famous paper by Von Neumann \[8\]. In this paper Von Neumann established an
inequality which he thought gave a dynamical foundation to quantum ergodic theory. In a series of papers \[9–12\] the results of Von Neumann were strongly criticized and in particular in \[12\] it was shown that the Von Neumann inequality was entirely a consequence of the averaging over “macro-observers” and has nothing to do with quantum dynamics. It is not our purpose here to discuss why all previous numerous attempts \[8–14\] to prove the quantum ergodic theorem failed. It was not even clear how to formulate the problem, and different ways had been proposed to circumvent the difficulty in formulating a quantum parallel of the classical ergodic theorem; namely, the fact that when the system is in an energy eigenstate, the probabilities do not change in time. For an extensive discussion we refer to \[13,14\] and to the more recent review by Pechukas \[15\]. In conclusion, the problem was left open: the main point is that all previous attempts did not call into question the structure of the eigenfunctions themselves, which is instead the crucial issue. In other words, in the computations of time-averages, the structure of the hamiltonian and therefore the dynamics, did not enter!

We now have a much better understanding of the dynamical properties of both classical and quantum systems. However, a critical re-examination of the fundamental hypothesis, as has been made in classical mechanics after the work of FPU, has not yet been made in quantum mechanics. This is quite surprising, especially in consideration of the increasing interest in the so-called “quantum chaos”, which deals mainly with the properties of quantum systems which are classically chaotic. In this respect a large number of papers is devoted to correlation properties of levels, periodic orbit theory and the like, but, as far as we know, a critical reexamination of the foundations of quantum statistical mechanics has not yet been undertaken \[16\]. For example, it is interesting that, while the justification of the microcanonical ensemble in classical mechanics has been the object of lively debates for almost one century, in quantum mechanics, as we have seen, the microcanonical ensemble is simply assumed and the only justification remains a hand-waving analogy with classical ergodicity and the agreement with experiments.

First of all, it is now clear that the existence of N-dimensional invariant surfaces in
classical systems implies restrictions on the quantum wavefunctions. Certainly, while an invariant KAM (after Kolmogorov, Arnold, Moser) curve constitutes an impenetrable barrier for the classical orbit, in quantum mechanics there is tunneling outside the invariant curves; however this tunneling is typically exponentially small and the situation is quite similar to the classical one. Therefore, the different complex problems generated by the presence of a divided phase space in classical mechanics, must also be taken into account in quantum mechanics. In particular, the lack of equipartition in classical mechanics implies a corresponding deviation from the expected equilibrium quantum statistical distributions. That is, the equilibrium properties will depend, as in classical mechanics, on the initial state.

However, our main interest here is in systems which are classically ergodic. In the following we will show that, besides classical ergodicity, additional conditions must be satisfied by the quantum Hamiltonian for the validity of equilibrium quantum statistical distributions. As a matter of fact, there is no reason to believe that the ergodicity of a classical system can be taken as justification for the assumption of a priori equiprobability in quantum mechanics. On the contrary, the so-called quantum dynamical localization, which is one of the main modifications imposed by quantum mechanics on classical chaotic motion, seems to point in the opposite direction. This phenomenon was discovered 20 years ago in the model of the kicked rotator [1,19] and has now been observed in several laboratory experiments [20–23]. It consists in the suppression of the diffusion process generated by classical chaotic motion and parallels the well-known Anderson localization. The crucial difference is that, in contrast to Anderson localization, it takes place in systems without any disorder in the Hamiltonian. More recently, dynamical localization has also been shown to take place in conservative systems [25,28–30]. For recent reviews see also [1,26]. It is our purpose to understand how dynamical localization manifests itself in systems of type (1.1), classically ergodic, and what is the relation of this new recently discovered phenomenon with the problem at hand.
III. LOCALIZATION IN QUANTUM HAMILTONIAN SYSTEMS

In order to approach this problem conveniently, let us analyze a model of conservative systems introduced by Wigner \[27\] and known as the Wigner Band Random Matrix (WBRM) model. Namely, we consider an ensemble of real Hamiltonian matrices of a rather general type:

\[
H_{mn} = \epsilon_n \delta_{mn} + v_{mn} \quad (m, n = 1, \ldots, N)
\]

where the off-diagonal matrix elements \(v_{mn} = v_{nm}\) are statistically independent, Gaussian random variables, with \(<v_{mn}>=0\) and \(<v_{mn}^2>=v^2\), if \(|m-n| \leq b\), and are zero otherwise.

The WBRM (3.1) provides a good description of the quantum statistical properties of general Hamiltonian systems of type (1.1) and therefore their consideration is very appropriate for the purposes of our discussion. The matrix (3.1) is given in the basis of unperturbed eigenstates \(\phi_n\) of \(\hat{H}_0\). Although in completely integrable quantum systems there is a quantum number for each degree of freedom, we suppose that the unperturbed states are ordered according to increasing energy, and we thereby label them with a single number \(n\). We denote by \(\rho\) the average density of states

\[
\rho^{-1} = \langle \epsilon_n - \epsilon_{n-1} \rangle
\]

where the averaging is understood either over disorder or within a single, sufficiently large, matrix. Both ways are equivalent owing to the assumed independence of matrix elements.

Let us consider the EF matrix \(C_{mn}\), which connects exact eigenfunctions \(\psi_m\), obtained by diagonalization of the Hamiltonian matrix (3.1), to unperturbed basis states \(\phi_n\),

\[
\psi_m = \sum_n C_{mn} \cdot \phi_n
\]

From the matrix \(C_{mn}\) we can compute both the statistical distribution \(W_m(n) = C_{mn}^2\) of the eigenstates \(\psi_m\) on the unperturbed ones \(\phi_n\), and the distribution \(w_n(m)\) of the unperturbed eigenstates on the exact ones. These distributions have classical analogs \(W\) and \(w\). Indeed, in the classical case, the unperturbed energy \(E_0\) is not constant along a classical chaotic
trajectory of the full Hamiltonian with a given total energy \( H = E \). Instead, it sweeps a range of values, or “energy shell”, \( \Delta E_0 = \Delta V \), and is distributed inside this shell according to a measure \( W_E(E_0) \). The form of \( W_E(E_0) \) depends on the form of the perturbation \( V \); we will call this measure “ergodic” because it is determined by the ergodic (microcanonical) measure on the given energy surface \( H = E \). The quantum analog of this measure characterizes the distribution of the “ergodic” eigenfunction in the unperturbed basis. Conversely, if we keep the unperturbed energy \( E_0 \) fixed, the bundle of trajectories of the total Hamiltonian \( H \), which reach the surface \( H_0 = E_0 \), has a distribution in the total energy \( E \) which is described by a measure \( w_{E_0}(E) \). In the quantum case, this measure corresponds to the energy spectrum of the Green’s function at energy \( E_0 \). It is also called the local spectral density of states (LDOS) \( w_{E_0}(E) \) or strength function or spectral measure of the unperturbed eigenstate at energy \( E_0 \). For a typical perturbation, represented by a WBRM, the average \( w(E) = \langle w_{E_0}(E) \rangle \) depends on the Wigner parameter

\[
q = \frac{(\rho v)^2}{b}
\]  

and has the following limiting forms [27] (see also Refs. [26,28])

\[
w(E) = \begin{cases} 
\frac{2}{\pi E_{sc}} \sqrt{E_{sc}^2 - E^2}, & |E| \leq E_{sc}, \quad q \gg 1 \\
\frac{\Gamma/2\pi}{E^2 + 1^2/4} \cdot \frac{\pi}{2 \arctan (1/\pi q)}, & |E| \leq E_{BW}, \quad q \ll 1
\end{cases}
\]  

Outside the specified energy intervals, both distributions have exponentially small tails. In the limit \( q \gg 1 \) we have the semicircle law with a width of the energy shell \( \Delta E = 2E_{sc} = 4v\sqrt{2b} \). In the other limit, \( q \ll 1 \), we have the Breit - Wigner distribution, of width \( \Delta E = 2E_{BW} = 2b/\rho \) with the main part of the distribution inside a width \( \Gamma = 2\pi \rho v^2 \). In all these expressions \( E \) is measured with respect to the center of the distribution.

The phenomenon of localization is related to the possibility that the eigenfunctions are localized on a scale which is significantly smaller than the maximum one consistent with energy conservation. Indeed, the localization length, namely the size of the region which is populated by an eigenfunction, is bounded from above by the \textit{ergodic localization length}
\( d^{(e)} = c \rho \Delta E \), which measures the maximum number of basis states coupled by the perturbation. This length characterizes the full width of the energy shell \( \Delta E \). (The factor \( c \) depends on the particular definition of localization width). In other words, in a conservative quantum system there is always localization in energy, due to the existence of a finite \( \Delta E \) \[25\]. This fact, which is sometimes a source of confusion, is just a trivial consequence of energy conservation. What is physically relevant is the possibility to have localization \textit{inside} the shell \[25\]. This possibility depends on a scaling parameter \( \lambda \) which we call the “ergodicity parameter”. Indeed, in \[25\] it was shown that the average localization length \( d \) of eigenfunctions defined as \( d \equiv \langle (\sum_n W^2_m(n))^{-1} \rangle \) (inverse participation ratio) obeys a scaling law of the form

\[
\beta_d = \frac{d}{d^{(e)}} \approx 1 - e^{-\lambda}
\]

where

\[
\lambda = \frac{ab^2}{d^{(e)}} = \frac{ab^{3/2}}{\rho v}
\]

Here \( a \approx 0.23 \) \[29\]. The parameter \( \lambda \) plays the role of an \textit{ergodicity parameter} because, when it is large, the localization length approaches its maximal value \( d^{(e)} \), which means that the eigenfunctions become ergodic, i.e., delocalized over the whole energy shell. Instead, if \( \lambda << 1 \), the eigenfunctions are strongly localized inside the energy shell. Notice that the matrix size \( N \) is an irrelevant parameter, provided \( N \gg d^{(e)} \) is large enough to avoid boundary effects.

In fig(1) we show a typical example of a localized eigenfunction(solid line). This figure is obtained \[29\] from a single matrix with parameters \( N = 2400, \ v = 0.1, \ b = 10, \ \rho = 300 \). In order to suppress fluctuations in individual distributions, averages have been taken over 300 of them, chosen around the center of the spectrum. The solid line is obtained by averaging with respect to the center of each eigenfunction so that the typical structure of the eigenfunction is revealed. The center is defined as:

\[
n_c(m) = \sum_n W_m(n)n
\]
The circles are obtained instead by averaging the same eigenfunction with respect to the center of the energy shell namely counting the site label in $W_m(n)$ starting from the reference site $m$ (instead of $n_c(m)$). As discussed in [29], this second type of average is expected to agree with the LDOS.

As is seen in fig. (1), the actual width of the eigenfunction is much less than the width of the LDOS which gives the maximum number of unperturbed states that can be coupled by the perturbation. This means that the eigenfunction is not ergodic.

Even though the analysis presented in this section is based on a random matrix model of a conservative system, the results remain qualitatively the same for real quantum conservative systems. Indeed it is now well established that the mechanism of localization inside the energy shell is quite typical and it was recently shown to take place e.g. in a classically chaotic billiard [30].

IV. QUANTUM STATISTICAL DISTRIBUTIONS

In the previous section we have shown that occurrence of dynamical localization in Hamiltonian systems leads to a deviation from ergodicity. A similar non ergodic quantum behaviour takes place when quantizing non ergodic classical systems. Indeed, if there are invariant regions of positive measure on the energy surface, such as invariant tori, then the range of values of $E_0$ swept by a classical orbit will be much narrower, or “localized” inside the classical energy shell and will moreover depend on initial conditions. In such a situation for example, the classical Maxwell Boltzmann distribution will not follow. For exactly the same reason, the equilibrium quantum statistical distribution is not to be expected in the presence of quantum localization independently of whether the latter is produced by purely dynamical quantum effects or by the presence of islands of stability in the classical phase space. In conclusion, even if the classical system is ergodic and mixing, the phenomenon of quantum localization do indeed provide reasons to reject the notion that the equal a priori probability is a non arbitrary postulate which agree with the correspondence principle. The
quantum steady state will depend on the initial conditions and only in the classical limit will approach the microcanonical distribution in accordance with the correspondence principle.

In order to explicitly show the mechanism through which quantum localization prevents the derivation of quantum statistical distributions, let us consider one of the standard methods \[31\] (see also \[32\]) to derive equilibrium distributions:

The average occupation number, \( n_s \), is given by

\[
\bar{n}_s(E) = \frac{\sum_\ell n_s(\ell) W_E(E_\ell)}{\sum_\ell W_E(E_\ell)} \quad (4.1)
\]

In order to compute the above average, according to \[31\], one introduces the sum extended over all states except state \( s \): \( Z_{E}^{s}(N) = \sum_\ell W_E(E_\ell) \). Then, in Fermi Dirac case \((n_s = 0, 1)\) for example, one obtains

\[
\bar{n}_s(E) = \frac{0 + Z_{E-\epsilon s}^{s}(N - 1)}{Z_{E-\epsilon s}^{s}(N - 1) + Z_{E}^{s}(N)} = \frac{1}{1 + Z_{E}^{s}(N)/Z_{E-\epsilon s}^{s}(N - 1)} \quad (4.2)
\]

Since the numbers of terms in the sum for the partition function is large, one can write

\[
\ln Z_{E-\epsilon s}^{s}(N - 1) = \ln Z_{E}^{s}(N) - \alpha_s - \beta_s \epsilon_s \quad (4.3)
\]

where \( \alpha_s = \frac{\partial \ln Z_{E}^{s}(N)}{\partial N} \), \( \beta_s = \frac{\partial \ln Z_{E}^{s}(N)}{\partial E} \). This leads to

\[
\bar{n}_s(E) = \frac{1}{1 + e^{\alpha_s + \beta_s \epsilon_s}}. \quad (4.4)
\]

Now, since the sum defining \( Z_{E}^{s}(N) \) is over many states, one expects that the parameters \( \alpha_s \) and \( \beta_s \) are insensitive as to which particular state \( s \) is omitted from the sum and therefore one can assume

\[
\alpha_s = \alpha; \beta_s = \beta = \frac{1}{T}. \quad (4.5)
\]

Then (4.4) gives the well known Fermi Dirac distribution.

However, in case of quantum localization, not only are the eigenfunctions localized inside the shell, but, as clearly evident from fig. 2, their centers are scattered inside the shell namely they change in a discontinuous way on moving from one eigenfunction to the next.
In such a situation the derivate $\frac{\partial \ln Z}{\partial E}$ does not even exist and the equilibrium distribution will depend on initial excitation. Notice that for classically chaotic conservative systems like billiards, the situation is even worse. Indeed in such cases it is clearly seen [33] that both the perturbed and unperturbed eigenfunctions have a sparse structure and this makes even more evident the impossibility to derive quantum equilibrium distributions. The same conclusions will follow when localization is produced by the lack of classical ergodicity: namely, by the existence of islands of stability in classical phase space (in this case too, temperature cannot be defined).

We would like to stress that the shape of the LDOS as well as its width is not relevant for the problem discussed here. As a matter of fact, for general Hamiltonian systems of type (1), the LDOS is not given by eq.(3.5) and the function $W_E(E_0)$ depends on the perturbation $V$. This perturbation can be very small so that the total energy $H = E$ can be very close to the unperturbed energy $H_0 = E_0$. In spite of this fact, in case of ergodicity the orbit of system (1) will move on the whole $2N - 1$ dimensional energy surface while the unperturbed integrable motion will take place on the N-dimensional torus. Analogously, in the quantum case, what is relevant is whether or not the perturbation actually couples the maximal numbers of unperturbed states: namely, whether or not the eigenfunctions are extended over the whole energy shell. Therefore, the relevant parameter is $\lambda$; for $\lambda > 1$ one expects Fermi-Dirac (or Bose-Einstein) statistics to hold. Instead, if $\lambda < 1$, one expects deviations from equilibrium statistical distributions and strong dependence on initial conditions.

Another question concerns the number of degrees of freedom. One lesson we have learnt from the study of dynamical chaos is that the so-called thermodynamical limit is not necessary: statistical laws can appear in systems with very few degrees of freedom, provided they are ergodic and mixing. We argue that quantum statistical distributions will take place even in systems with few degrees of freedom, provided dynamical localization is absent, namely $\lambda > 1$. Finally we would like to remark that for classically ergodic systems the ergodicity parameter $\lambda$ always becomes larger than one in the semiclassical limit, as required by the
correspondence principle.

V. CONCLUSIONS

In this paper we have attempted to elucidate the problem of the foundations of quantum equilibrium statistical distributions at the light of recent progress in nonlinear dynamics and in quantum chaos. In particular we have shown that in presence of quantum dynamical localization the equilibrium state depends on the initial excitation and does not obey the standard quantum statistical distributions. The corresponding problem of energy equipartition in classical mechanics has been, at the very start of this century, at the root of the transition to the quantum theory. More recently, the discovery of FPU and KAM, that below a certain threshold the ergodic hypothesis is not valid and therefore energy equipartition among different degrees of freedom does not follow, has made a significant impact in our understanding of physical systems. It is possible that a critical re-examination of the analogous problem in quantum mechanics, in order to justify quantum equilibrium distributions, may lead to interesting developments for our understanding of the microscopic world.
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FIG. 1. Structure of a localized eigenfunction for a single matrix with parameters $N = 2400$, $v = 0.1$, $b = 10$, $\rho = 300$, $q = 90$. The fat full line is the semicircle law (3.5). The solid line was obtained by averaging 300 eigenfunctions with respect to their centers; circles, by averaging the same eigenfunctions with respect to the centers of their energy shells. Here the parameter $\lambda = 0.24$, and the average with respect to centers $n_c(m)$ of the distributions $W_m(n)$ shows a clear localization with $\beta = 0.24$, while the other average(circles) remains close to semicircle, with $\beta = 0.99$. 
FIG. 2. A comparison of the structure of eigenfunctions and of LDOS in the localized case of fig.1. Solid vertical bars represent the widths $\Delta n$ of individual eigenfunctions over the unperturbed basis. Horizontal dotted lines show the size $\Delta m$ of the local spectrum for individual basis states. Although all basis states have comparable sizes, close to the size of the energy shell, they are very sparse ($\beta = 0.20$), due to the fact that EF’s are strongly localized, and irregularly scattered inside the energy shell.