

Unitarity, ergodicity, and quantum thermodynamics

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Abstract. This paper is concerned with the ergodic subspaces of the state spaces of isolated quantum systems. We prove a new ergodic theorem for closed quantum systems which shows that the equilibrium state of the system takes the form of a grand canonical density matrix involving a complete commuting set of observables including the Hamiltonian. The result obtained, which is derived for a generic finite-dimensional quantum system, shows that the equilibrium state arising from unitary evolution is always expressible in the canonical form, without the consideration of a system-bath decomposition.

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Given the Hamiltonian \hat{H} and the initial state $|\psi_0\rangle$ of an isolated quantum system, what is the dynamic average

$$\langle\langle \hat{O} \rangle\rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \langle \psi_s | \hat{O} | \psi_s \rangle ds \quad (1)$$

of an observable \hat{O} when the state $|\psi_t\rangle = e^{-i\hat{H}t}|\psi_0\rangle$ of the system evolves unitarily? Is there an equilibrium density matrix $\hat{\rho}$, with a thermodynamic characterisation, such that the average is given by $\langle\langle \hat{O} \rangle\rangle = \text{tr}(\hat{\rho}\hat{O})$?

In the case of a classical system, if the Hamiltonian evolution is ergodic, then the theorem of Koopman, von Neumann, and Birkhoff shows that the dynamic average can be replaced by a statistical average over a subspace of the phase space determined by the relevant conservation laws [1]. If the system consists of a large number of interacting particles, then the dynamic average is intractable, whereas the statistical average in many cases can be calculated.

In the case of quantum systems, while the equilibrium properties of small subsystems of large systems have been studied extensively [2, 3, 4, 5, 6, 7, 8, 9, 10, 11], less attention has been paid to the equilibrium states arising as a consequence of the unitary evolution of closed systems. The purpose of this paper is to investigate such systems and to derive rigorous results concerning (a) the dynamic averages of observables, and (b) the associated equilibrium states.

We consider an isolated quantum system based on a Hilbert space of dimension $n+1$, with a generic, nondegenerate Hamiltonian \hat{H} (the degenerate case will be considered later). We write $\{E_i\}_{i=0,1,\dots,n}$ for the energy eigenvalues, and $\omega_{ij} = E_i - E_j$ for the eigenvalue differences. The normalised energy eigenstates will be denoted $\{|E_i\rangle\}_{i=0,1,\dots,n}$, with the associated projection operators $\{\hat{\Pi}_i\}_{i=0,1,\dots,n}$. We write $|\psi_0\rangle$ for the initial state, and $\{|\psi_t\rangle\}_{0 \leq t < \infty}$ for its unitary evolution under the influence of \hat{H} . With these definitions at hand, the main result can be expressed as follows:

Quantum ergodic theorem. *The dynamic average of an observable \hat{O} is given by $\langle\langle \hat{O} \rangle\rangle = \text{tr}(\hat{\rho}\hat{O})$, where*

$$\hat{\rho} = \frac{1}{Z(\beta, \{\mu_i\})} \exp\left(-\beta\hat{H} - \sum_{i=2}^n \mu_i \hat{F}_i\right), \quad (2)$$

and $Z(\beta, \{\mu_i\}) = \text{tr} \exp(-\beta\hat{H} - \sum_{i=2}^n \mu_i \hat{F}_i)$. Here \hat{H} together with $\{\hat{F}_i\}_{i=2,\dots,n}$ constitute a complete set of commuting observables. The effective inverse temperature β and chemical potentials $\{\mu_i\}_{i=2,\dots,n}$ are given by the relations

$$\beta = \frac{\partial S}{\partial E}, \quad \text{and} \quad \mu_i = \frac{\partial S}{\partial F_i}, \quad (3)$$

where $E = \text{tr}(\hat{\rho}\hat{H})$, and $F_i = \text{tr}(\hat{\rho}\hat{F}_i)$. The entropy $S = -\text{tr}(\hat{\rho} \ln \hat{\rho})$ is given by

$$S = -\sum_{i=0}^n p_i \ln p_i, \quad (4)$$

with $p_i = |\langle \psi_0 | E_i \rangle|^2$.

The appearance of the grand canonical density matrix (2) is surprising, since this structure normally arises with the consideration of the equilibrium thermodynamics of a small system immersed in a thermal bath. Indeed, the canonical form $\hat{\rho} = \exp(-\beta\hat{H})/Z(\beta)$ is known to appear in the case of a system in a thermal bath for an overwhelming majority of wave functions of the total system [10, 11]. Equation (2) is a stronger result, valid in the case of a closed system, involving no approximations and no invocation of the thermodynamic limit.

To determine the equilibrium states of a closed quantum system we need to identify the subspaces of the quantum state space over which a generic time evolution will exhibit ergodicity. The idea is that in general there are n conserved quantities arising in connection with unitary evolution in a Hilbert space of dimension $n+1$. These are given by the expectation values of n linearly independent observables that commute with the Hamiltonian, one of these being the Hamiltonian itself. Writing E for the expectation of \hat{H} , we can then write $\{F_i\}_{i=2,\dots,n}$ for the expectation values of the other members of the commuting set, which we denote by $\{\hat{F}_i\}_{i=2,\dots,n}$. By fixing the expectation values of these conserved quantities we are left with a set of n relative-phase degrees of freedom for the state vector that span the ergodic subspace of the state space associated with the given initial state.

We shall show that the equilibrium state corresponds to a uniform distribution over the toroidal subspace of the quantum state space spanned by the relative phases. The

equilibrium distribution is characterised, in particular, by a density-of-states function Ω , which acts as a measure of the size of the toroidal subspace. The associated density matrix $\hat{\rho}$ is given by the von Neumann-Lüders state; that is to say,

$$\hat{\rho} = \sum_{i=0}^n p_i \hat{\Pi}_i, \quad (5)$$

where $p_i = |\langle \psi_0 | E_i \rangle|^2$. This might be surprising, since such a state arises most naturally in the context of measurement theory, where it describes the state of a system after an energy measurement has been performed. The result is consistent with the fact that the time average of the dynamics of the density matrix under unitary evolution is given by the von Neumann-Lüders state. It follows that the dynamic average (1) of an arbitrary observable \hat{O} is given by $\text{tr}(\hat{\rho}\hat{O})$.

To identify the ergodic subspaces of the quantum state space, we first consider the example of a two-level system, with $n = 1$. The one-parameter family of states generated by unitary evolution can be written in the form

$$|\psi_t\rangle = \cos \frac{1}{2} \theta |E_1\rangle + \sin \frac{1}{2} \theta e^{i(\phi + \omega_{10}t)} |E_0\rangle, \quad (6)$$

where $0 \leq \theta \leq \pi$ and $0 \leq \phi < 2\pi$. The pure state space has the geometry of a sphere, and unitary evolution gives rise to a rigid rotation of the sphere around the axis determined by the two energy eigenstates. Given the initial state $|\psi_0\rangle$, the dynamical trajectory is the latitudinal circle on which $|\psi_0\rangle$ lies. The circle is fixed by setting the initial energy E of the system, which is the only conserved quantity. Every point on the latitudinal circle is traversed by the dynamical trajectory, which makes this circle the ergodic subspace of the state space. The dynamic average of an observable can thus be replaced by the ensemble average with respect to a uniform distribution over the circle.

To calculate the associated density of states we compute the weighted volume in the pure state manifold occupied by the states having the given property. In general, if we have a set of conserved quantities $\{G_j\}_{j=1,\dots,m}$ given by $G_j = \langle \psi_t | \hat{G}_j | \psi_t \rangle$, then the associated density of states is

$$\Omega(\{G_j\}) = \int \prod_{j=1}^m \delta(\langle \psi | \hat{G}_j | \psi \rangle - G_j) dV_\psi, \quad (7)$$

where the integration is over the space of pure states and dV_ψ is the associated volume element. The corresponding construction for classical systems is considered in [12], where $\Omega(\{G_j\})$ is referred to as a “substructure function”. In the case of a two-level system the ergodic circle is chosen by fixing the expectation of the Hamiltonian: $E = \langle \hat{H} \rangle$. In terms of the spherical coordinates (θ, ϕ) of (6), the constraint can be written in the form $(E_1 - E_0) \cos^2 \frac{1}{2} \theta = E - E_0$. We thus integrate $\delta(\cos^2 \frac{1}{2} \theta - (E - E_0)/(E_1 - E_0))$ over the pure state manifold. Since the volume element is $dV = \frac{1}{4} \sin \theta d\theta d\phi$, the resulting density of states is

$$\Omega(E) = \mathbf{1}_{\{E_0 < E < E_1\}} \frac{\pi}{E_1 - E_0}, \quad (8)$$

where $\mathbf{1}_{\{A\}}$ denotes the indicator function: $\mathbf{1}_{\{A\}} = 1$ if A is true and $\mathbf{1}_{\{A\}} = 0$ otherwise.

We proceed to calculate the density of states for $n = 2$. In this case there are two conserved quantities: $E = \langle \hat{H} \rangle$ and $F = \langle \hat{F} \rangle$, where the observable \hat{F} commutes with \hat{H} , but is not of the form $a\hat{H} + b\hat{1}$. The calculation simplifies if we use an equivalent set of constraints obtained by fixing the expectation values of two of the energy projectors, say, $p_0 = \langle \hat{\Pi}_0 \rangle$ and $p_1 = \langle \hat{\Pi}_1 \rangle$. It follows from the resolution of identity that $p_2 = \langle \hat{\Pi}_2 \rangle = 1 - p_0 - p_1$. The unitary trajectory can be written in the form

$$|\psi_t\rangle = \sin \frac{1}{2} \theta_1 \cos \frac{1}{2} \theta_2 |E_2\rangle + \sin \frac{1}{2} \theta_1 \sin \frac{1}{2} \theta_2 e^{i(\phi_1 + \omega_{21}t)} |E_1\rangle + \cos \frac{1}{2} \theta_1 e^{i(\phi_2 + \omega_{20}t)} |E_0\rangle, \quad (9)$$

and the two constants of motion are given by $p_0 = \cos^2 \frac{1}{2} \theta_1$ and $p_1 = \sin^2 \frac{1}{2} \theta_1 \sin^2 \frac{1}{2} \theta_2$, which fix the variables θ_1, θ_2 . Therefore, under a generic unitary evolution the ergodic subspace of the quantum state space is the two-torus \mathcal{T}^2 spanned by ϕ_1, ϕ_2 . The density of states is obtained by integrating $\delta(\cos^2 \frac{1}{2} \theta_1 - p_0) \delta(\sin^2 \frac{1}{2} \theta_1 \sin^2 \frac{1}{2} \theta_2 - p_1)$ over the pure state manifold, with the appropriate volume element, which in this case is $dV = \frac{1}{32} \sin \theta_1 (1 - \cos \theta_1) \sin \theta_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2$. Performing the relevant integration we find that $\Omega(p_0, p_1) = \pi^2$ in the triangular region $\{0 < p_0, p_1 < 1\} \cap \{0 < p_0 + p_1 < 1\}$, and vanishes otherwise.

In the case of a general $(n + 1)$ -level system there are n conserved quantities associated with unitary dynamics. It follows that under a generic time evolution for which the eigenvalue differences $\{\omega_{ij}\}$ are incommensurate the typical ergodic subspace of the quantum state space is given by an n -torus \mathcal{T}^n . To calculate the density of states $\Omega(p_0, \dots, p_{n-1})$ we fix the constraints $\langle \hat{\Pi}_i \rangle = p_i$ for $i = 0, \dots, n - 1$, express these in terms of the coordinates (θ_i, ϕ_i) , and perform the constrained volume integral over the pure state manifold by using the volume element

$$dV = 2^{-n} \prod_{i=1}^n \cos \frac{1}{2} \theta_i \sin^{2i-1} \frac{1}{2} \theta_i d\theta_i d\phi_i. \quad (10)$$

The result is

$$\Omega(p_0, \dots, p_{n-1}) = \pi^n \quad (11)$$

in the hyper-triangular region $\{0 < p_0, \dots, p_{n-1} < 1\} \cap \{0 < p_0 + \dots + p_{n-1} < 1\}$, and $\Omega(p_0, \dots, p_{n-1}) = 0$ otherwise. We see that irrespective of the Hilbert space dimensionality the density of states is constant in the hyper-triangular region, and is independent of the energy E and the conserved quantities $\{F_i\}_{i=2, \dots, n}$.

The analysis above leads to the following observation. Since for each n we have identified the ergodic subspaces of the state space, we are able to apply Birkhoff's theorem to conclude that the dynamic average of an observable can be replaced by the statistical average of the observable with respect to an equilibrium state given by a uniform distribution over the toroidal subspace \mathcal{T}^n .

To compute the expectation of an observable \hat{O} we determine the density matrix associated with the equilibrium distribution over the state space. We remark in this connection that the density matrix associated with a probability density function on the pure state manifold is the expectation of the pure-state projection operator with

respect to that density function. Now in the energy basis a pure-state projector can be expressed in the form

$$|\psi\rangle\langle\psi| = \sum_{i,j} \sqrt{p_i p_j} e^{i(\phi_i - \phi_j)} |E_i\rangle\langle E_j|. \quad (12)$$

Thus, the diagonal elements $\{p_i\}$ of the pure-state projector are real, whereas the off-diagonal elements contain phase factors. The equilibrium distribution has fixed values for the $\{p_i\}$ and a uniform distribution over the phase variables. It follows that if we take the average of the projector $|\psi\rangle\langle\psi|$ over the phases, the off-diagonal elements drop out and we are left with the von Neumann-Lüders state (5).

The appearance of the von Neumann-Lüders density matrix as the equilibrium state is consistent with the fact that the dynamic average of the density matrix is itself given by the von Neumann-Lüders state. This can be seen as follows:

$$\begin{aligned} \langle\hat{\rho}\rangle &= \lim_{t \rightarrow \infty} \frac{1}{t} \sum_{i,j} \int_0^t \hat{\Pi}_i e^{-i\hat{H}s} \hat{\rho}_0 e^{i\hat{H}s} \hat{\Pi}_j ds \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \sum_{i,j} \hat{\Pi}_i \hat{\rho}_0 \hat{\Pi}_j \int_0^t e^{-i\omega_{ij}s} ds \\ &= \sum_i \hat{\Pi}_i \hat{\rho}_0 \hat{\Pi}_i + \lim_{t \rightarrow \infty} \sum_{i \neq j} \hat{\Pi}_i \hat{\rho}_0 \hat{\Pi}_j \frac{1 - e^{-i\omega_{ij}t}}{i\omega_{ij}t} \\ &= \sum_i \hat{\Pi}_i \hat{\rho}_0 \hat{\Pi}_i = \sum_i p_i \hat{\Pi}_i. \end{aligned} \quad (13)$$

In particular, we see that the timescale involved for the averaging to become effective is determined by the energy differences. We thus conclude that the dynamic average of an observable \hat{O} is given by $\text{tr}(\hat{\rho}\hat{O})$, where $\hat{\rho}$ is given by (5). This representation of the density matrix, however, does not make the thermodynamic properties of the equilibrium state immediately apparent. We shall demonstrate, however, that in association with the conserved quantities $(E, \{F_i\})$ there is a corresponding system of conjugate variables $(\beta, \{\mu_i\})$ that can be given a consistent thermodynamic interpretation. In the case of the energy the conjugate variable has the interpretation of the inverse temperature. For the other observables the associated conjugate variables can be interpreted as chemical potentials. This suggests that the equilibrium state arising from unitarity and ergodicity might be of a grand canonical type. The conjugate variables are defined as follows. Writing (5) for the density matrix associated with the toroidal subspace characterised by the conserved quantities $(E, \{F_i\})$ we have $\text{tr}\hat{\rho} = 1$, $\text{tr}(\hat{\rho}\hat{H}) = E$, and $\text{tr}(\hat{\rho}\hat{F}_k) = F_k$. Let us define a family of $n + 1$ operators $\{\hat{G}_i\}_{i=0,1,\dots,n}$ by setting $\hat{G}_0 = \hat{1}$, $\hat{G}_1 = \hat{H}$, and $\{\hat{G}_i\}_{i=2,\dots,n} = \{\hat{F}_i\}_{i=2,\dots,n}$, writing $\{G_i\}_{i=0,1,\dots,n}$ for the corresponding expectation values with respect to $\hat{\rho}$, so $G_0 = 1$, $G_1 = E$, and $\{G_i\}_{i=2,\dots,n} = \{F_i\}_{i=2,\dots,n}$. In other words, $\text{tr}(\hat{\rho}\hat{G}_i) = G_i$ for $i = 0, 1, \dots, n$. It follows from (5) that

$$\sum_{i=0}^n p_i \text{tr}(\hat{\Pi}_i \hat{G}_j) = G_j. \quad (14)$$

Thus, writing $g_{ij} = \text{tr}(\hat{\Pi}_i \hat{G}_j)$ and defining h_{jk} by $\sum_{j=0}^n g_{ij} h_{jk} = \delta_{ik}$, we see that

$$p_k = \sum_{j=0}^n G_j h_{jk}, \quad (15)$$

and therefore that

$$\hat{\rho} = \sum_{j,k=0}^n G_j h_{jk} \hat{\Pi}_k. \quad (16)$$

To verify that h_{jk} exists, we observe that if it did not, then there would exist a nonzero vector ξ_i such that $\sum_{j=0}^n g_{ij} \xi_j = 0$; but that would imply $\text{tr}(\hat{\Pi}_i \sum_{j=0}^n \hat{G}_j \xi_j) = 0$ for all i , and hence $\sum_{j=0}^n \hat{G}_j \xi_j = 0$, contrary to the assumption that the \hat{G}_j are linearly independent.

Formula (16) gives $\hat{\rho}$ as a function of E and $\{F_i\}$. Therefore, writing $S = -\text{tr}(\hat{\rho} \ln \hat{\rho})$ for the entropy, we obtain an expression for S as a function of E and $\{F_i\}$. The associated conjugate variables are then defined by the thermodynamic relation

$$dS = \beta dE + \sum_{k=2}^n \mu_k dF_k, \quad (17)$$

where β is the effective inverse temperature and $\{\mu_k\}$ are the effective chemical potentials. This shows, on account of the linear independence of the observables, the equivalence of the specification of either (i) the initial state $|\psi_0\rangle$ up to relative phases, (ii) the probabilities $p_i = |\langle \psi_0 | E_i \rangle|^2$, (iii) the expectation values E and $\{F_i\}$, or (iv) the conjugate variables β and $\{\mu_i\}$. We can therefore investigate how the equilibrium density matrix (5) can be expressed either in terms of the extensive variables E and $\{F_i\}$, or in terms of the conjugate variables β and $\{\mu_i\}$.

For the various representations of the density matrix we consider first the example of the two-level system. In this case we solve the relations $p_0 + p_1 = 1$ and $p_0 E_0 + p_1 E_1 = E$ for the diagonal elements p_0, p_1 of $\hat{\rho}$, and obtain

$$\hat{\rho}(E) = \begin{pmatrix} \frac{E_1 - E}{E_1 - E_0} & 0 \\ 0 & \frac{E - E_0}{E_1 - E_0} \end{pmatrix}. \quad (18)$$

Computing the entropy and using the relation $dS = \beta dE$ we can express the inverse temperature as a function of E . The result is

$$\beta(E) = \frac{1}{E_1 - E_0} \ln \left(\frac{E_1 - E}{E - E_0} \right). \quad (19)$$

By inverting this relation, we then obtain

$$E(\beta) = \frac{E_0 e^{-\beta E_0} + E_1 e^{-\beta E_1}}{e^{-\beta E_0} + e^{-\beta E_1}}. \quad (20)$$

Expression (20) is, however, the expectation of the energy with respect to the canonical density matrix. That is to say, (18) can be expressed in the form

$$\hat{\rho}(E) = \frac{1}{Z(\beta)} \begin{pmatrix} e^{-\beta E_0} & 0 \\ 0 & e^{-\beta E_1} \end{pmatrix}, \quad (21)$$

where $Z(\beta) = e^{-\beta E_0} + e^{-\beta E_1}$. The important point here is that the inverse temperature β is not specified exogenously via the introduction of a heat bath. Rather, it is defined endogenously, through the specification of the energy of the equilibrium state associated with the given initial state.

Let us now turn to the proof of the quantum ergodic theorem in the general case. It follows from (16) that the entropy is given by

$$S = - \sum_{k=0}^n \left(\sum_{j=0}^n G_j h_{jk} \right) \ln \left(\sum_{j=0}^n G_j h_{jk} \right). \quad (22)$$

Thus, defining $\gamma_i = \partial S / \partial G_i$ by use of this expression, we find that

$$\gamma_i = - \sum_{k=0}^n h_{ik} \left[\ln \left(\sum_{j=0}^n G_j h_{jk} \right) + 1 \right] = - \sum_{k=0}^n h_{ik} (\ln p_k + 1), \quad (23)$$

by (15), and hence

$$\begin{aligned} \ln p_i + 1 &= - \sum_{j=0}^n g_{ij} \gamma_j = - \sum_{j=0}^n \text{tr} \left(\hat{\Pi}_i \hat{G}_j \right) \gamma_j \\ &= - \gamma_0 - \gamma_1 \text{tr} \left(\hat{\Pi}_i \hat{H} \right) - \sum_{j=2}^n \gamma_j \text{tr} \left(\hat{\Pi}_i \hat{F}_j \right). \end{aligned} \quad (24)$$

Setting $\gamma_1 = \beta$ and $\{\gamma_i\}_{i=2,\dots,n} = \{\mu_i\}_{i=2,\dots,n}$, these relations are then sufficient to determine the diagonal elements $\{p_i\}_{i=0,\dots,n}$ of the equilibrium density matrix in terms of the intensive variables, and we are led to the grand canonical ensemble (2) with the identification $\gamma_0 = \ln Z - 1$. The effective inverse temperature, however, is not associated with an external heat bath, but rather is intrinsic to the system, and a similar remark applies to the effective chemical potentials. The fact that the conjugate variables are determined endogenously shows that our result does not require an assumption of entropy maximisation.

In the case of a degenerate Hamiltonian, the ergodic subspace of the state space is contracted to a smaller torus $\mathcal{T}^m \subset \mathcal{T}^n$, where $m + 1$ is the number of distinct energy eigenvalues. This follows from the fact that since some of the eigenvalue differences ω_{ij} vanish, only m of the n relative phases for the unitary trajectory $|\psi_t\rangle$ vary in time. As a consequence, we need only to consider $m - 1$ independent observables $\{\hat{F}_i\}$ whose eigenspaces coincide with that of the Hamiltonian. In other words, there are only m terms, given by \hat{H} and $\{\hat{F}_i\}_{i=2,\dots,m}$, in the exponent of (2) for the grand canonical density matrix. As an example consider the case of a three-dimensional Hilbert space where the energy eigenvalues are given by E_0 , E_1 , and E_1 . The elements of the density matrix are $p_0 = (E_1 - E)/(E_1 - E_0)$ and $p_1 = p_2 = (E - E_0)/2(E_1 - E_0)$. A short calculation making use of the relation $dS = \beta dE$ then shows that

$$E(\beta) = \frac{E_0 e^{-\beta E_0} + 2E_1 e^{-\beta E_1}}{e^{-\beta E_0} + 2e^{-\beta E_1}}, \quad (25)$$

which is evidently the expectation of \hat{H} with respect to the canonical density matrix $\hat{\rho} = \exp(-\beta \hat{H}) / \text{tr} \exp(-\beta \hat{H})$.

A challenging open issue is to understand the implications of the quantum ergodic theorem for macroscopic systems. In the case of a large quantum system the energy spectrum of a typical model Hamiltonian is highly degenerate. As a consequence, the number of independent macro-observables \hat{H} and $\{\hat{F}_i\}$ required for the exact specification of the equilibrium density matrix is significantly reduced. For real systems, however, due to the complexity of internal interactions one would expect the degeneracies in model Hamiltonians to split into closely located but distinct levels. Therefore, the specification of a small number of macro-variables will only provide an approximate description of the equilibrium state for real systems. On the other hand, if there are large clusters of observables with the property that in the equilibrium state defined by (2) the chemical potentials are approximately equal, then the resulting state can be adequately characterised by a small number of macro-variables, and thus can be regarded as effectively classical. It is interesting in this connection to contrast the results obtained here for quantum systems with the corresponding results for strictly classical systems: While ergodicity is generic for quantum systems, classically it is exceptional [13]. The fact that the characterisation of the equilibrium state of a quantum system is simpler, and that the equilibrium distribution can be derived dynamically by use of an ergodicity argument, might be related to the special structures of energy surfaces in quantum phase spaces [14].

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