Thermalization of isolated quantum many-body system and entanglement

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Abstract

Thermalization of an isolated quantum system has been a non-trivial problem since the early days of quantum mechanics. In generic isolated systems, non-equilibrium dynamics is expected to result in thermalization, indicating the emergence of statistical mechanics from quantum dynamics. However, what feature of many-body quantum system facilitates quantum thermalization is still not well understood. Here we revisit this problem and show that introduction of entanglement in the system gives rise to thermalization, and it takes place at the level of individual eigenstate. We also show that the expectation value in the energy eigenstate of each subsystem is close to the canonical average.

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1. INTRODUCTION

A prerequisite for statistical mechanics is the maximization of entropy in a system at thermal equilibrium. In other words, when a system gets thermalized one can find out the values of corresponding physical observables and thermodynamic functions from its statistical description or representative ensemble. However, an isolated quantum many-body system initialized in a pure state remains pure during unitary evolution, and in this sense it has zero entropy. Then, what is the mechanism through which such a quantum system, whose initial state is pure, gets thermalized and quantum statistical mechanics emerges from it? Thermalization of an isolated quantum system and emergence of statistical ensembles from its unitary time evolution has been a fascinating problem since the early days of quantum mechanics [1–5]. In the classical scenario, the assumption of ergodicity leads to statistical mechanics. However, the notion of ergodicity adopted for classical systems has failed in leading to similar conclusion in the quantum regime despite numerous attempts [1, 6, 7]. Most of the works have emphasized the need of coupling with an external heat bath [8], which is being done traditionally, in order to obtain statistical mechanics. Later, it has been shown that a finite but very small perturbation may lead to such a temporal evolution of the system that time average of observables are in agreement with the microcanonical ensemble, commonly known as eigenstate thermalization hypothesis (ETH) [3, 4]. The name itself signifies that thermalization happens at the level of individual eigenstates.

In the last decade, experimental developments [9–15] have made precise simulation of unitary evolution of many-body quantum systems and important experimental studies of thermalization possible, stimulating theoretical interest. Discussion about those theoretical works is beyond the scope of this paper, however, one can find those in [5, 16–18] and the references therein.

A generic isolated many-body quantum system thermalize to a microcanonical distribution consistent with their energy density [16], and the experimental results are consistent with this fact. The mechanism behind this is the eigenstate thermalization, as prescribed by eigenstate thermalization hypothesis. Though ETH successfully describes the thermalization of a generic isolated system, integrable systems possessing extensive sets of non-trivial conserved quantities do not follow it. As a result, in general, integrable system do not thermalize [17], rather they do equilibrate. To describe such intergrable systems after equilibration generalized Gibbs ensembles (GGEs) are used [18]. In the last few years, a lot of research has been carried out to understand the thermalization of both integrable and non-integrable systems. However, what feature of many-body quantum system helps in quantum thermalization is not clear yet. Recently, experimental studies [19] with ultra-cold atoms have confirmed that entanglement [20–22] acts as a thermalizing agent in isolated quantum many-body systems. The confirmation comes from the simultaneous measurement of entanglement entropy [23, 24] and thermal averages of observables of the sub-systems. As the system’s state, initialized in a pure one, moves towards thermal equilibrium, its entanglement entropy starts to grow. The growth of entanglement entropy with respect to time and size of the subsystems has been studied in [19]. Later, using standard quasiparticle picture the entanglement dynamics in the space-time scaling limit has been studied [25].

In this article, we focus on two facts; firstly, a generic isolated many-body quantum system thermalizes according to ETH, and secondly, entanglement can facilitate thermalization in such a system. We show that the knowledge of a single entangled state of the global system is sufficient to compute two thermal averages, microcanonical and canonical. Our result depicts that entanglement not only drives an isolated many-body quantum system towards thermal equilibrium, it also helps in thermalization at the level of individual eigenstate.

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The rest of the article is arranged as follows: In Section (II), we briefly review the eigenstate thermalization of generic isolated many-body quantum systems. Section (III) demonstrates our findings. Finally, in Section (IV) we conclude our work.

II. EIGENSTATE THERMALIZATION OF GENERIC ISOLATED QUANTUM SYSTEM

First introduced by Deutsch[3] and coined by Srednicki[4], ETH aims to recover the results of quantum statistical mechanics from a closed quantum system. For this purpose a small perturbation Hamiltonian \( \hat{H}_{int} \), in the form of a random matrix, is added to the system, and the system is allowed to evolve under the total Hamiltonian \( \hat{H} = \hat{H}_0 + \hat{H}_{int} \). Here, \( \hat{H}_0 \) is the Hamiltonian of the system. At first glance it seems that due to the external perturbation, the system having a well defined energy may cause macroscopic fluctuation in its energy. However, it can be easily shown that after the perturbation has been turned off the ratio \( \Delta E / E \) decreases as \( 1/\sqrt{N} \), where \( \Delta E \) is the spread of the total energy \( E \) and \( N \) is the degrees of freedom. Therefore, the eigenstate occupation probabilities remain localized around a small range of energies. The elements of \( \hat{H}_{int} \) are chosen from a random Gaussian ensemble, and in the basis of the eigenvectors of \( \hat{H}_0 \) these are represented as,

\[
h_{ij} = \langle E_i | \hat{H}_{int} | E_j \rangle, \quad \langle h_{ij} h_{kl} \rangle = \epsilon^2 \delta_{ik} \delta_{jl} \]

Such a modelling of the perturbation Hamiltonian yields that in the limit of large \( N \), small but finite \( \epsilon \) will couple many neighbouring levels within the range \( E \) and \( E \pm \Delta E \). This coupling between energy levels occurs because at fixed energy per particle, the separation between levels decreases exponentially with \( N \) and becomes arbitrarily small. The number of energy levels in the window \( \Delta E \) is proportional to \( \Delta E \exp[\mathcal{S}(E)] \), \( \mathcal{S}(E) \) being the total entropy at total energy \( E \), and there is a large range of values for \( \epsilon \) which will couple these large number of levels. It is expected that for large \( N \), the coupling energy \( \epsilon \) can be made much smaller than the energy per particle, and have a large effect on eigenvectors. The eigenvectors of \( \hat{H} \) should then coherently mix the eigenvectors of \( \hat{H}_0 \) within a window \( \Delta E \). This mixing of the unperturbed eigenvectors finally gives rise to ergodicity.

Let, \( |\psi_i\rangle \) be an eigenvector of total Hamiltonian \( \hat{H} \), \( \{|\phi_j\rangle | j = 1 \text{ to } N \} \) be the eigenvectors of unperturbed Hamiltonian \( \hat{H}_0 \) and the initial state of the system be,

\[
|\Psi\rangle = \sum_{i=1}^{N} C_i |\psi_i\rangle
\]  

where, \( \sum_i |C_i|^2 = 1 \). Then, ETH[3] implies

\[
\langle \langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}} = \langle \hat{A} \rangle_{\text{micro}}
\]

In Eq.(3) averaging of the expectation value is done over different realizations of \( \hat{H}_1 \). From this equation it is clear that thermalization happens at the level of individual eigenstates. The variance \( \Delta A^2 \), which can be written as \( \Delta A^2 \equiv \langle \langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}} - \langle \langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}}^2 \), decreases exponentially with \( N \). Therefore, in the limit of large \( N \),

\[
\langle \Psi | \hat{A} | \Psi \rangle_{t} = \sum_i |C_i|^2 \langle \hat{A} \rangle_{\text{micro}}
\]

\[
= \langle \hat{A} \rangle_{\text{micro}}
\]

Given the mechanism of thermalization of an isolated quantum many-body quantum system, one question naturally arises: what should be the property or properties of the system due to which thermalization will take place following that mechanism? In[4], it has been shown that a closed quantum many-body system will thermalize according to eigenstate thermalization if Berry’s conjecture[26] holds for that system. On the other hand, Berry’s conjecture is found to be valid for eigenstates of sufficiently high energy in classical chaotic systems. Therefore, the implication of the validity of this conjecture for an isolated quantum system is that it has to be chaotic.

Let, the state of such a chaotic quantum system at any instant of time \( t \) is

\[
|\Psi_t\rangle = \sum_{i=1}^{N} C_i e^{-iE_it} |\psi_i\rangle
\]

where, \( E_i \) denote the energy eigenvalue corresponding to the eigenstate \( |\psi_i\rangle \) of \( \hat{H} \). If \( \hat{A} \) be an observable of interest, then infinite time average of its expectation value is

\[
\bar{A} \equiv \lim_{t \rightarrow \infty} \frac{1}{t} \int_{0}^{t} A_{t} \, dt
\]

\[
= \sum_i |C_i|^2 A_{ii}
\]

\( A_t \) is the expectation value of the observable at time \( t \), given by

\[
A_{t} = \langle |\Psi_{t}\rangle | \hat{A} | \Psi_{t} \rangle
\]

\[
= \sum_{ij} C_i^* C_j e^{i(E_j - E_i)t} A_{ij}
\]

In order show that \( A_t \) is equal to the thermal average , it is assumed that in a chaotic quantum system the matrix elements of \( \hat{A} \) take the form[27]

\[
A_{ij} = \mathcal{A}(E) \delta_{ij} + e^{-S(E)/2} f(E, \omega) R_{ij}
\]

where, \( E \equiv \frac{1}{2} (E_i + E_j) \), \( \omega \equiv (E_i - E_j) \), and \( S(E) \) is the thermodynamic entropy at energy \( E \), given by

\[
e^{S(E)} \equiv E \sum_i \delta(E - E_i)
\]

the functions \( f(E, \omega) \) and \( \mathcal{A}(E) \) are smooth functions of their arguments. \( R_{ij} \) is a numerical factor that varies
erratically with $i$ and $j$. Detailed discussion about these functions is beyond the scope of this paper. However, here we focus on few things \cite{27} that will serve the purpose. First of all, Eq.\,(9) is semiclassical in nature and the factor of $e^{-S(E)/2}$ scales like $\hbar^{(N-1)/2}$. Thus for the validity of this equation $\hbar$ has to be small, which in practice requires that energy $E$ must be large. Secondly, the general structure described by Eq.\,(9) is preserved under multiplication \cite{27}, implying the generic character of the equation. As a result, the validity of this equation guarantees the validity of the following expression for the matrix elements of any power of $A$,

$$
(A^n)_{ij} = \mathcal{A}_n(E) \delta_{ij} + e^{-S(E)/2} f_n(E, \omega) R_{ij}^{(n)}
$$

(11)

Thirdly, the function $\mathcal{A}(E)$ can be related to the canonical thermal average of $A$ as,

$$
\mathcal{A}(E) = \langle \hat{A} \rangle_{\text{can}} + \mathcal{O}(N^{-1}) + \mathcal{O}(e^{-S/2})
$$

(12)

Finally, using Eqs.\,(6-12) and considering few physical conditions one can show that at thermal equilibrium $\hat{A} = \langle \hat{A} \rangle_{\text{can}}$.

III. RESULTS

Let the initial Hamiltonian of an isolated quantum many-body system be $\hat{H}_0$ and the dimension of its Hilbert space be $N$. Without loss of generality we can map the many-body system to a two-body system, $S$ and $R$. Therefore, the initial Hamiltonian can be split as $\hat{H}_0 = \hat{H}_S \otimes \hat{1}_R + \hat{1}_S \otimes \hat{H}_R$. The structure of the eigenstates forming the eigenbasis of $\hat{H}_0$ is as follows:

$$
|\phi_{lk}\rangle = |\alpha_l\rangle \otimes |\beta_k\rangle
$$

$$
\hat{H}_S|\alpha_l\rangle = a_l|\alpha_l\rangle \quad l = 1, \ldots, n
$$

$$
\hat{H}_R|\beta_k\rangle = b_k|\beta_k\rangle \quad k = 1, \ldots, m
$$

$$
\hat{H}_0|\phi_{lk}\rangle = (a_l + b_k)|\phi_{lk}\rangle
$$

(13)

In the last equation we introduce a new index $j$ such that it is in a one-to-one correspondence with the original index $(l, k)$. Thus the eigenbasis of the non-interacting Hamiltonian consists of $N$ eigenstates, each being denoted as $|\phi_j\rangle$, where $j = 1, \ldots, nm$ and $nm = N$. Let $E$ be the mean energy of the system. With the hope of making the system obey quantum statistical mechanics a small perturbation $\hat{H}_{\text{int}}$ is added to it. We leave the details of each element of $\hat{H}_{\text{int}}$, and just assume that due to this external perturbation entanglement is established between the energy eigenstates of $S$ and $R$. Before the application of the perturbation let the total system be in an eigenstate of the non-interacting Hamiltonian $\hat{H}_0$. Instead of raising the initial product state of the system, say with energy $E_j$, to an excited state having energy $E_{j+1}$, where $E_{j+1} > E_j$, the external perturbation couples the energy eigenstates of the subsystems. The total Hamiltonian of the system is now $\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}$ and the system evolves under this Hamiltonian. The eigenvectors forming the eigenbasis of $\hat{H}$ are the entangled states $|\psi_i\rangle$.

Let, $\hat{H}_0$ and $\hat{H}$ be the Hilbert spaces corresponding to the isolated system before and after the application of the external perturbation. The basis vectors of these two spaces are related as

$$
|\psi_i\rangle = \sum_j p_{ij}|\phi_j\rangle
$$

(14)

which means that $i^{th}$ eigenstate of $\hat{H}$ is a coherent mixture of the eigenstates of $\hat{H}_0$; in other words, any basis vector of $\hat{H}$ is a linear combination of the basis vectors of $\hat{H}_0$. Normalization condition requires $\sum_j |p_{ij}|^2 = 1$. Thus the transformation of energy eigenstates due to the external perturbation can be viewed as a linear mapping between the two mentioned Hilbert spaces, and the elements of the matrix representing the map are the complex entities $p_{ij}$. Let us denote the transformation matrix as $P$, and assume it to be a random unitary matrix. The matrix corresponding to the inverse map will therefore be $P^\dagger$, because for unitary matrix $P^\dagger = P^{-1}$. From the structure of $|\phi_j\rangle$ one can easily verify that the state $|\psi_i\rangle$ in the above equation is an entangled one. In the next we show the revival of the results of quantum statistical mechanics.

A. Microcanonical average

As we want to show that due to entanglement the isolated system will move towards thermal equilibrium, we need to look on the variation in the expectation value of an observable in an energy eigenstate,

$$
\langle \psi_i| \hat{A} |\psi_i\rangle = \sum_{\nu\mu} p_{\nu\mu} p_{ij} \langle \phi_\nu| \hat{A} |\phi_\mu\rangle
$$

(15)

In the limit of large $N$ there will be numerous energy levels in the window $\Delta E$ having different eigenstates. Therefore, the expectation value will vary from state to state. In such a case variance is a good measure to find out how the expectation value in an eigenstate differs from a mean value. For this we first calculate the average value of $\langle \psi_i| \hat{A} |\psi_i\rangle$. We find (See Appendix)

$$
\langle \langle \psi_i| \hat{A} |\psi_i\rangle \rangle_{\text{rand}} = \sum_j \frac{1}{N} \langle \phi_j| \hat{A} |\phi_j\rangle
$$

(16)

The right hand side of the above equation represents microcanonical average of $\hat{A}$. Using the postulates of quantum statistical mechanics we can effectively write the state of an isolated system as

$$
|\psi\rangle = \sum_{j=1}^N p_j |\phi_j\rangle
$$

(17)
where, $|p_j|^2 = 1$ in the energy window of $\Delta E$ and zero elsewhere. If $\rho$ is the density matrix representing the microcanonical ensemble, then $|p_j|^2$ are its diagonal elements. Typically, these diagonal elements are function of energy, but here we just focus on its generic character. Thus the observed value of $\hat{A}$ for this system is given by

$$\langle \hat{A} \rangle_{\text{micro}} = \langle \psi | \hat{A} | \psi \rangle = \frac{\sum_j |p_j|^2 \langle \phi_j | \hat{A} | \phi_j \rangle}{\sum_j |p_j|^2} = \frac{1}{N} \sum_j |\langle \phi_j | \hat{A} | \phi_j \rangle|$$

(18)

Hence, we find that the average of the expectation value of observable $\hat{A}$ in an eigenstate of the global system is equal to $\langle \hat{A} \rangle_{\text{micro}}$, i.e.,

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle_{\text{rand}} = \langle \hat{A} \rangle_{\text{micro}}$$

(19)

The variance is found to be

$$\Delta \hat{A}^2 = \langle \langle \psi | \hat{A} | \psi \rangle^2 \rangle_{\text{rand}} - \langle \langle \psi | \hat{A} | \psi \rangle \rangle_{\text{rand}}^2 \leq \frac{1}{N} \langle \hat{A}^2 \rangle_{\text{micro}}$$

(20)

Till now what we find is that in the limit of large $N$ the fluctuation in the expectation value of observable $\hat{A}$ in an energy eigenstate of interacting Hamiltonian becomes negligible, and the expectation value remains equal to the microcanonical average.

To find out the time average of the expectation value, let us consider an arbitrary initial state of the system,

$$|\Psi\rangle = \sum_i C_i |\psi_i\rangle$$

(21)

This state is evolving unitarily under the action of total Hamiltonian $\hat{H}$. In the interacting basis the time average of the expectation of $\hat{A}$ can be shown to be

$$\langle \langle \Psi | \hat{A} | \Psi \rangle \rangle_t = \lim_{T \to \infty} \frac{1}{N} \int_0^T \langle \Psi | \hat{A} | \Psi \rangle dt = \sum_i \langle \langle \psi_i | \Psi \rangle^2 \langle \psi_i | \hat{A} | \psi_i \rangle$$

(22)

Now substituting Eq.(14) for $|\Psi\rangle$ and averaging as before we get two terms. One of these vanishes in the limit of large $N$ and we finally get,

$$\langle \langle \Psi | \hat{A} | \Psi \rangle \rangle_t \equiv \langle \hat{A} \rangle_{\text{micro}}$$

(23)

B. Canonical average

Now we consider an arbitrary observable $\hat{M}$ of the subsystem $S$ and find out the expectation value of this observable. It is assumed that the dimension of $S$ is much smaller than that of $R$. Let us express an eigenstate of Hamiltonian $\hat{H}$ as,

$$|\psi\rangle = \sum_i^{n} \sum_{k=1}^{m} p_{ik}|\alpha_i \rangle \otimes |\beta_k\rangle$$

(24)

Then the expectation value is

$$\langle \psi | \hat{M} \otimes 1_R | \psi \rangle = \sum_{i,\nu=1}^{n} \sum_{k=1}^{m} p_{ik}^* p_{\nu k} M_{\nu}$$

(25)

From quantum mechanical principles we have,

$$\langle \psi | \hat{M} \otimes 1_R | \psi \rangle = \text{Tr}(\hat{M} \rho_S)$$

(26)

where, $\rho_S$ is the state of system $S$ after doing partial trace on the eigenstate $|\psi\rangle$, i.e., $\rho_S = \text{Tr}_R(|\psi\rangle\langle \psi|)$. As every eigenstate of $\hat{H}$ is entangled, state of subsystem $S$ is mixed and diagonal in its eigenbasis. The diagonal elements are the terms $|p_{ik}|^2$, which are generally functions of energy$^{28, 29}$. However, we do not express the elements $p_{ik}$ explicitly in terms of energy. Rather, we use the result of $^{30}$, where it has been shown that using Levy’s lemma$^{31}$ one can prove that $p_{ik} \equiv \exp(-\beta E_i)$ for the condition $m >> n$ (the dimension of the subsystem $R$ is larger than that of $S$), where $Z = \sum_i \exp(-\beta E_i)$. The Gibb’s form$^{32}$ of density matrix depends on the nature of coupling between $S$ and $R$; for weak coupling $\rho_S = \exp(-\beta \hat{H}_S)/Z$, whereas, for strong coupling $\rho_S = \exp(-\beta \hat{H}_S^*)/Z^*$, where $\hat{H}_S^*$ is the Hamiltonian of mean force$^{33, 34}$. Hence, for a generic state of $S$ we have,

$$\text{Tr}(\rho_S) = \sum_i^n \rho_{ii} M_{ii}$$

$$= \frac{\text{Tr}(\rho_S)}{\text{Tr}(\rho_S)} \equiv \langle M \rangle_{\text{can}}$$

(27)

IV. CONCLUSION

We have revisited the problem of thermalization of a generic isolated many-body quantum system and shown that establishment of entanglement in the system leads to thermalization, which is in confirmation with experimental evidence$^{19}$. According to ETH ergodicity arises due to coupling of neighbouring energy levels in the window $\Delta E$ or coherent mixing of eigenstates of unperturbed Hamiltonian $\hat{H}_0$. We have looked on this mixing of eigenstates from a different perspective. In a quantum many-body system, when there is no interaction between the subsystems, an eigenstate of $\hat{H}_0$ is basically a product state, where the components of the product are the eigenstates of the subsystems. Now, when these product states mix coherently then the resulting state is an entangled
state, and also an eigenstate of the interacting Hamiltonian $H$. We have considered one such entangled eigenstate and analyzed the expectation value of an observable $\hat{A}$ in that state. What we have found is that entanglement not only gives rise to thermalization, it thermalizes the system according to eigenstate thermalization. We show that in the limit of large $N$ the fluctuation in the expectation value in an eigenstate becomes negligibly small and the expectation value is equivalent to microcanonical average. Our result shows that the time average of expectation value is also equivalent to microcanonical average. Basically, time averaging plays auxiliary role; thermalization happens at the level of individual eigenstates and expectation value of an observable is equivalent to its equilibrium value in any eigenstate. To check the equivalence between expectation value of an observable and canonical average we consider an observable of a subsystem and find its expectation value. As the global pure system gets entangled, the initial pure state of any subsystem becomes mixed, which becomes clear when we take partial trace to find the density matrix system becomes mixed, which becomes clear when we take partial trace to find the density matrix $\rho_S$. Experimentally, the same fact has been observed, entanglement starts to grow after a quench is applied on a closed and pure many-body quantum system and destroys the purity of the subsystems. The subsystems become mixed and their mixedness can be quantified by the second-order Rényi entropy as $S(2) = -\log[\text{Tr}(\hat{\rho})] [19]$. Instead of determining the elements of $\rho_S$ explicitly as function of energy we have used the known result: if $S$ and $R$ are entangled, and dimension of $R$ is much larger than that of $S$ then $\rho_S \equiv \rho_{\text{can}}$. Using this fact we have found that the expectation value of observable $M$ is equivalent to canonical average. Previous theoretical works[17] also noticed the relation between entanglement and thermalization of an isolated quantum system by finding that the function $f(E, \omega)$ in Eq.(9) carries multiparticle entanglement structure of the energy eigenstates. We hope that our work will shed light on the role of entanglement energetics in the thermalization of an isolated many-body quantum system, thereby paving the path for better understanding of quantum thermodynamics[35–42].

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## Appendix

### A. Microcanonical average

Let us consider the $i^{th}$ eigenstate of Hamiltonian $\hat{H}$ as given in Eq.(14). The expectation value of an observable $\hat{A}$ in this state is given by Eq.(15). Before finding the average of the expectation value, let us focus on the inverse mapping of the Hilbert spaces $\mathcal{H}_0$ and $\mathcal{H}$. As we have assumed that the transformation matrix $P$ is a random unitary matrix, from the properties of unitary matrices we have $P^{-1} = P^\dagger$, where $P^\dagger$ denotes complex conjugation. Thus from Eq.(14) we can write

$$|\phi_j\rangle = \sum_i p_{ji}|\psi_i\rangle \quad (28)$$

and from the orthonormality of the basis systems we have $\sum_i |p_{ji}|^2 = 1$. Now keeping the $i^{th}$ eigenstate fixed, but averaging over its different realization, we get the average of the expectation value as

$$\langle\langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}} = \frac{1}{N} \sum_{i} \sum_{\mu\nu} p_{i\mu}^* p_{i\nu} \langle \phi_\nu | \hat{A} | \phi_\mu \rangle$$

$$= \frac{1}{N} \left( \sum_{i} \sum_{\mu=\nu} |p_{i\mu}|^2 \langle \phi_\nu | \hat{A} | \phi_\nu \rangle + \sum_{i} \sum_{\mu=\nu} p_{i\mu}^* p_{i\nu} \langle \phi_\nu | \hat{A} | \phi_\mu \rangle \right)$$

$$= \frac{1}{N} \left( \sum_{i} |p_{i1}|^2 \langle \phi_1 | \hat{A} | \phi_1 \rangle + \sum_{i} |p_{i2}|^2 \langle \phi_2 | \hat{A} | \phi_2 \rangle + \ldots + \sum_{i} |p_{iN}|^2 \langle \phi_N | \hat{A} | \phi_N \rangle \right)$$

$$= \sum_j \frac{1}{N} \langle \phi_j | \hat{A} | \phi_j \rangle \quad (29)$$

The right-hand side of the above equation is equivalent to microcanonical average as depicted in Eq.(18).

### B. Variance in expectation value

The variance of expectation value of $\hat{A}$ is

$$\Delta \hat{A}^2 = \langle\langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}} - \langle \langle \psi_i | \hat{A} | \psi_i \rangle \rangle_{\text{rand}}^2$$

The first term on the right-hand side can be evaluated by substituting Eq.(14) for $|\psi_i\rangle$ and averaging as before.
We have,
\[
\langle \psi_i | \hat{A} | \psi_i \rangle^2_{\text{rand}} = \sum_{j,k,l,m} (p_{ij}^* p_{ik} p_{kl}^* p_{lm})_{\text{rand}} \times \langle \psi_j | \hat{A} | \psi_k \rangle \langle \psi_j | \hat{A} | \psi_m \rangle
\]
\[
= \frac{1}{N^2} \sum_i \left\{ \sum_j |p_{ij}|^4 \langle \psi_j | \hat{A}^2 | \psi_j \rangle + \sum_{j,l} |p_{ij}|^2 |p_{il}|^2 \langle \psi_j | \hat{A} | \psi_l \rangle \langle \psi_l | \hat{A} | \psi_j \rangle + \sum_{j,k,l,m} p_{ij}^* p_{ik} p_{kl}^* p_{lm} \langle \psi_j | \hat{A} | \psi_k \rangle \langle \psi_l | \hat{A} | \psi_m \rangle \right\}
\]
\[
= (30)
\]

After expanding the summations in the above equation and inserting the expression for variance we finally get Eq.(20),
\[
\Delta \hat{A}^2 \leq \frac{2}{N^2} \sum_j \langle \psi_j | \hat{A}^2 | \psi_j \rangle \leq \frac{2}{N} \langle \hat{A}^2 \rangle_{\text{micro}}
\]
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