Thermodynamic entropy of a many-body energy eigenstate

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Abstract. It is argued that a typical many-body energy eigenstate has a well-defined thermodynamic entropy and that individual eigenstates possess thermodynamic characteristics analogous to those of generic isolated systems. We examine large systems with eigenstate energies equivalent to finite temperatures. When quasi-static evolution of a system is adiabatic (in the quantum mechanical sense), two coupled subsystems can transfer heat from one subsystem to another and yet remain in an energy eigenstate. To explicitly construct the entropy from the wave function, degrees of freedom are divided into two unequal parts. It is argued that the entanglement entropy between these two subsystems is the thermodynamic entropy per degree of freedom for the smaller subsystem. This is done by tracing over the larger subsystem to obtain a density matrix and calculating the diagonal and off-diagonal contributions to the entanglement entropy.
1. Introduction

The main question investigated here is if it is possible to define a thermodynamic entropy for energy eigenstates of a generic many body system, and if so, how this can be characterized by examining the wave function in such a state. The thermodynamic entropy $S$ is measurable experimentally by changing parameters such as temperature $T$ and calculating small changes in heat $dQ$ via the relation

$$dS = \frac{dQ}{T}.$$  \hspace{1cm} (1)

By incrementally measuring $dS$ relative to a reference state, say at low temperature, the entropy can be calculated. The entropy is important because it is only a function of thermodynamic state variables, not a system’s history, and therefore it should be, in principle, calculable without changing external parameters. Classically, the Boltzmann hypothesis that the entropy is the logarithm of the number of states dynamically accessible to a system appears to be correct for generic systems in strict thermal equilibrium [1]. This gives a means to determine a system’s entropy with external parameters held constant.

In quantum mechanics, our understanding of entropy is not as well developed. A theoretical calculation of the entropy is possible via the free energy, using the canonical ensemble. An ensemble of systems is summed over, each one with a different energy. Although this appears to work in practice, the reason why this canonical entropy formula works for a pure state is not clear. The calculation assumes that the system is in a mixed state, with microcanonical or canonical weights.

The ensemble calculation of the entropy is not necessarily applicable to the calculation of the entropy in a pure state. The von Neumann entropy is commonly used for a system with a density matrix $\rho$ and is $S_{VN}(\rho) = -\text{tr} \rho \ln \rho$. $S_{VN}$ is zero for a system in a pure state, although it gives the usual result for the entropy using a canonical mixed state.
After the observation of an isolated system, it becomes in a pure state that is an eigenstate of the associated observable operator. But it is far from clear whether the canonical entropy calculation applies to such cases. However one expects that thermodynamics should apply to pure states, as the observation of isolated systems is commonly considered in thermodynamic contexts. However, because the von Neumann entropy is zero, it is hard to see how this definition of the entropy can be compatible with thermodynamics.

On the other hand, if we consider a system in an energy eigenstate, it has a trivial time dependence, and it is hard to see how to associate a thermodynamic entropy with it, in any way similar to the Boltzmann hypothesis. There is no exploring of phase space with time and it is not clear from our intuition of heat how the concept of entropy could be meaningful.

In many discussions in the literature, the entropy is taken to be the von Neumann entropy and it is not uncommon to see authors claiming that the ‘entropy’ of a pure state is zero, despite the fact that this does not appear to be consistent with the thermodynamic notion of entropy. This is a very fundamental issue that is clearly in need of further investigation, and this is what is done in this paper.

It is in fact possible, as we shall see below, to define thermodynamic entropy for a system in an energy eigenstate and show that this entropy is the same as the entropy calculated for an ensemble mixed state.

In this work, I consider a single energy eigenstate of a large ergodic system, with the word ‘ergodic’ defined in the next section. I argue that for such a state, the concept of a thermodynamic entropy is still meaningful and that such a system under extremely slow external perturbations such as a changing magnetic field will transfer heat between different parts of a system while remaining in an energy eigenstate in accordance with the usual laws of thermodynamics. The entropy transfer that appears is precisely the same as is calculated using the canonical ensemble.

The above result is suggestive, but does not prove that there exists a thermodynamic entropy that is a function of the energy eigenstate for a complete isolated system. This leaves open a very interesting question: if the state of the system determines the entropy, then there should be some way of obtaining that entropy directly from the wave function instead of by changing external parameters. This would be the analogue of the Boltzmann hypothesis in classical statistical mechanics. This recipe should for large system sizes give identical results to the ensemble calculation of the entropy.

To construct the entropy of an energy eigenstate, the quantity used is the ‘entanglement entropy’. First, we subdivide a system into two macroscopic systems, one labeled $\theta$ and the other labeled $\phi$ with $m$ and $n$ degrees of freedom, respectively. One first defines a density matrix $\rho_\phi = \text{tr}_\theta |\phi, \theta\rangle \langle \phi, \theta|$. Then the entanglement entropy $S_E \equiv -\text{tr} \rho_\phi \ln \rho_\phi$. This has many useful properties. For example, it is also equal to $-\text{tr} \rho_\theta \ln \rho_\theta$.

The entanglement entropy plays a crucial role in quantum information theory and has also been used in the study of black holes and quantum phase transitions. The entanglement entropy has been argued to be a unique measure of entanglement in a pure state by making analogies with thermodynamics, but its relationship to the thermodynamic entropy is still unclear.

At zero temperature, $S_E$ is nonzero but non-extensive and, for a variety of systems, is a power law of system size. At finite temperature and large system size, 1 + 1-dimensional quantum field theories give extensive behavior.
Here, we examine how to calculate the entanglement entropy in an energy eigenstate by similar means to those used earlier to investigate the question of energy eigenstate thermalization, which is explained in section 2. This is also a necessary assumption in the problem, discussed in section 3, of how thermodynamic entropy applies to energy eigenstates.

We argue that for a system in an energy eigenstate where the number of degrees of freedom $n_{\text{tot}}$ goes to infinity, and energies corresponding to a fixed finite temperature, there is a very interesting relation between the entanglement entropy $S_E$ and the thermodynamic entropy $S$. We divide a system into two pieces as mentioned above, of size $m$ and $n$, with $m > n$ and $m + n = n_{\text{tot}}$. For a homogeneous system, when $n/n_{\text{tot}} < 1/2$ the entanglement entropy $S_E = (n/n_{\text{tot}})S$. This gives an explicit formula for deducing thermodynamic properties from individual energy eigenstates. It is surprising that the derivation of this formula only breaks down when $n/m \geq 1$, where of course the roles of $m$ and $n$ can be switched. Thus, by calculating the entanglement entropy for a finite number of divisions (two or more) and summing over them, the thermodynamic entropy is recovered.

The outline of this paper is as follows. In section 2, we discuss previous work that argues that for energy eigenstates, the expectation value of a large class of observables will be equivalent to averages using the microcanonical ensemble. Using this, in section 3 we explore the relation between thermodynamic entropy and its microcanonical value, for systems in energy eigenstates. In section 4, we analyze the entanglement entropy using methods similar to those of section 2.

2. Energy eigenstate thermalization

Previous work by the present author [12] and others [13] attempted to understand why the laws of quantum statistical mechanics work for an isolated system. The approach taken was to see what could be derived about statistical mechanics from quantum mechanics without any additional assumptions and for a particular choice of model systems. The assumption made in quantum statistical mechanics is that the average over time $\langle \ldots \rangle_t$ of some observable quantity $\langle \psi | A | \psi \rangle$ is equal to a microcanonical average at a total energy $e$ that is assumed to be well defined (see below),

$$\langle \langle \psi | A | \psi \rangle \rangle_t = \sum_j \Delta(e, e_j) \langle j | A | j \rangle,$$  \hspace{1cm} (2)

where $e_j$ labels an energy eigenstate of the entire system and $\Delta(e, e_j)$ is a function that is sharply peaked at $e = e_j$. For a system containing a large number of degrees of freedom and for a large class of operators $A$, this can be written with negligible error in terms of the canonical distribution at fixed temperature (throughout this work, units are chosen so that Boltzmann’s constant is unity)

$$\langle \langle \psi | A | \psi \rangle \rangle_t = \frac{\sum_j e^{-e_j/T} \langle j | A | j \rangle}{\sum_j e^{-e_j/T}}.$$  \hspace{1cm} (3)

We will postpone to the end of this section how these formulae should, rather simply, be modified to take into account fluctuations in the total energy, but equation (2) or equivalently equation (3) has been enormously successful in explaining problems in almost every branch of physics. For the purposes of this paper, systems obeying this equation will be called ‘ergodic’.
In classical mechanics, a system with a few degrees of freedom such as Sinai billiards has time averages given by the microcanonical distribution. A quantum mechanical treatment of the same system cannot be expected to give the microcanonical distribution. It is easy to show by counterexample that one needs at least one more requirement: the number of degrees of the system must also be large. Indeed, if the spacing between energy levels is not small it is impossible to define a microcanonical distribution in a precise way.

Indeed, the density of states \( G(E) \) for a system with \( n \) degrees of freedom is related to the entropy, and for an extensive system, \( G(E) = (1/e_0) \exp(ns(E/n)) \). Here \( s \) is the entropy per particle and \( e_0 \) is an energy normalization. Therefore, if the energy width in the microcanonical average is \( \delta \), then the number of states being averaged over is proportional to \( \delta \exp(ns(E/n)) \). With fixed \( \delta \), the number of states contributing to the average diverges exponentially with \( n \), implying that fluctuations in microcanonical quantities will rapidly go to zero with increasing \( n \) as the total energy is varied.

Having a large number of degrees of freedom, however, is not enough to ensure ergodicity. As a simple example, consider a perfect harmonic crystal in which case the initial choice of wave function alters the time averages of an observable. If such a system were to start with a wave function obeying equation (2), then shining light on it so as to couple to some modes preferentially will now violate this microcanonical average.

Thus, we must search for a mechanism that can explain how an experimental system can continue to give microcanonical averages for time-averaged quantities despite atypical initial states, such as the example of light described above. The approach taken was similar to understanding how this works for an almost ideal classical gas. A genuine ideal gas has no interaction between different particles and therefore will not be ergodic, but can be made so by slight modification. For example, the particles can be given hard cores of very small diameter, which will have a negligible effect on the statistical and thermodynamic properties computed from the Gibbs distribution. However, after a long enough time, the system will explore almost all of its available phase space enabling the rigorous application of the statistical mechanical formula equation (2). In the same spirit, suppose we start with a Hamiltonian that decouples into \( n \) separate subsystems

\[
H_0 = \sum_{i=1}^{n} h_0(x_i, p_i). \tag{4}
\]

This system is not ergodic. However, the main result of the previous work [12] was to show that with negligible error in the limit of large \( n \), it can be made ergodic by the addition of a small perturbation as described below.

The model considered was

\[
H = H_0 + H_1, \tag{5}
\]

where \( H_1 \) is added in the hope of making the system ergodic. In the case of an ideal gas for example, one may want to add some interaction between the different particles; for example, take

\[
H_1 = \sum_{i<j}^{n} V(r_i - r_j). \tag{6}
\]

However, this is extremely hard to analyze, so instead of adding in these interactions explicitly, we use a random matrix model to understand the effects of a generic perturbation. If we
consider the problem in the basis of energy eigenvalues of $H_0$, then we model $H_1$ by a real symmetric matrix whose elements are chosen from a real random Gaussian ensemble, with certain physically sensible conditions on the magnitude of the elements described in the next paragraph. The use of a random matrix is sensible in this context as much work, starting with the monumental work of Wigner [14], has shown a deep connection between the physics of interacting systems and random matrices.

We take the variances of these random couplings to decrease away from the matrix diagonal:

$$h_{ij} = \langle E_i | H_1 | E_j \rangle, \quad h_{ij}h_{kl} = \epsilon_{i-j}^2 \delta_{ik} \delta_{jl},$$

where the magnitudes of the $\epsilon$ are taken to be much less than $T$ but much greater than the energy spacing as will be discussed in more detail below. In this paper, the line above the matrix elements denotes an average over the ensemble of random matrices.

The reason why the variance of the matrix elements is taken to depend on position is explained in more detail in appendix A, but in general, one expects asymptotically the effect of coupling from states of different energies $E_1$ and $E_2$ to decrease with their energy difference. The size of elements is diminished by a phase space factor

$$\langle E_1 | H_1 | E_2 \rangle \sim e^{-|E_1 - E_2|/T}$$

for $T \ll |E_1 - E_2| \ll E_1$ (the ground-state energy of the system is set as 0). The temperature is defined by the usual prescription

$$\frac{1}{T} = \frac{\partial S}{\partial E}.$$  \hfill (9)

The energy $E$ in the above derivative can be evaluated at either $E_1$ or $E_2$ since for a large system, $T \ll E$. So when $|E_1 - E_2| \gg T$, the proportion of nonzero matrix elements is effectively zero. To simplify the model further, we consider a banded random matrix, where the width of the band increases with energy. Inside the band, all off-diagonal elements have the same variance $\epsilon$. The precise form of the cut-off is unimportant for the conclusions but should be present on physical grounds and also prevents unphysical divergences in expectation values.

The random matrix model defined above is similar to the one analyzed by Wigner [15], where he considered a matrix with diagonal elements that were linearly increasing, $D_i = \Delta_1 i$, and $\Delta = 1/G(E)$ can be taken to be the average energy level spacing, and off-diagonal random matrix elements are banded as above with the width $n_b \gg 1$. Eigenvectors are random but the squares of the amplitudes are well defined and are not constant. Denoting the amplitudes of the $i$th eigenvector by $c_{ij}$,

$$\sigma_{ij} \equiv |c_{ij}|^2 = \frac{\epsilon^2}{(\Delta i - \Delta j)^2 + \delta^2},$$

where

$$\delta = \frac{\pi \epsilon^2}{\Delta},$$

for $|i - j| \Delta \ll n_b \Delta$. In the opposite limit, the eigenvalues decay faster than an exponential. That is why finite $n_b$ prevents unphysical divergences.

As it turns out, the width of the Lorentzian $\delta$ determines the energy width that is used when doing a microcanonical average in equation (2). Therefore one would like $\delta \ll T$, so as not to change the microcanonical result. But conversely, $\delta \gg \Delta$ (the energy spacing). Both
requirements are easily satisfied because, as mentioned above, the total number of states contributing to the microcanonical average is $\sim \delta \exp(ns(E/n))$. This means that one should choose $\Delta = \epsilon_0 \exp(-ns(E/n)) \ll \delta \ll T$, which is easily satisfied for large $n$, as we will take $\delta$ to be independent of $n$. In terms of the parameter $\epsilon$ in this model, equation (11) gives that $\Delta \ll \epsilon \ll \sqrt{T\Delta}$. Because of the immense smallness of $\Delta$, the addition of $\epsilon$ will not significantly change the partition function for this system. Instead, it was shown [12] that its effect is to make infinite time averages in accord with the microcanonical distribution.

The sense in which this model gives microcanonical results is as follows. One considers time averages done with one choice of random matrix. The answer will differ from that of another realization. We can compute what the variance of the average will be, averaged over all matrices in the ensemble. It was shown that this variance is proportional to $\Delta/\delta$, which is exponentially small in $n$.

The most striking feature of this is that the equivalence to the microcanonical distribution should apply even to energy eigenstates for a large class of operators $A$. This is surprising because the time dependence of such wave functions is trivial and therefore does not show any chaotic time-dependent behavior. Of course the spatial dependence is extremely complex and this is the reason why it can give rise to this kind of self-averaging. This equivalence for energy eigenstates has been recently confirmed by ab initio numerical tests [16] and is often referred to as ‘eigenstate thermalization’.

A caveat must be stated to the above claim. For an initial state with a large spread in total energies, the microcanonical distribution is not obtained because the system cannot be averaged at only one energy. Instead it can be shown [12] that time averages require an additional averaging, over the probability of finding the system at a particular energy.

### 3. Thermodynamics of energy eigenstates

An energy eigenstate has trivial time dependence and it is of interest to investigate whether a complete system when placed in such a state still obeys thermodynamics. For an isolated system, there is no heat flow into or out of the system, so we examine a closed system composed of two macroscopic parts $A$ and $B$ that are weakly interacting so that the Hamiltonian is $H = H_A + H_B + H_i$. To analyze this, we will assume the thermalization of individual eigenstates [12], as argued in the last section.

Suppose only $H_A$ depends on an external parameter, $x$. For example, $x$ could be an external magnetic field or the position of a piston. Because $H_B$ does not depend on the external parameter, one could regard $B$ as a heat bath for subsystem $A$, although this would only be a good analogy when subsystem $B$ was much larger than $A$. For example, $A$ could be a gas cylinder with a movable piston at position $x$, and $B$ could be a heat bath in contact with $A$. We can analyze how energy gets transferred between $A$ and $B$ as a result of changing $x$ infinitesimally and quasi-statically from $x$ to $x + dx$. By ‘quasi-static’, we mean adiabatic in the quantum mechanical sense. We are also considering a completely isolated system, so that it is adiabatic in the thermodynamic sense. However, the subsystems can transfer energy between each other.

Because we are only interested in systems that are not integrable (and in fact ‘ergodic’ in the sense of the word given above), we expect that energy level repulsion will prevent any level crossing during a change in $x$, so it is possible, in principle, to vary a parameter and stay in an energy eigenstate.
Since in an energy eigenstate $E$ depends on $x$, by the Guttinger–Feynman–Hellman theorem [17],
\[ \frac{\partial E}{\partial x} = \langle \psi | \frac{\partial H}{\partial x} | \psi \rangle. \] (12)

Because of our assumption of individual eigenstate thermalization,
\[ \frac{\partial E}{\partial x} = \langle \frac{\partial H}{\partial x} \rangle_m = \langle \frac{\partial H_A}{\partial x} \rangle_m, \] (13)
where the subscript $m$ under the averages denotes a microcanonical average. The right-hand side implies that the energy derivative is the same as for a generic mixed state (with the usual assumption of a sharply peaked energy distribution). Because for a large system the microcanonical average is equivalent to a canonical average, and the average only involves subsystem $A$, we take the average over only subsystem $A$ using, say, a microcanonical ensemble for $A$. Therefore it is possible to relate this to the microcanonical (or canonical) definition of entropy in $A$ similar to standard procedures, see for example [18].

Firstly, the work $dW$ done by the system when $x$ is changed quasi-statically to $x + dx$ is
\[ dW = - \frac{\partial E}{\partial x} dx. \] (14)

Note that the rate must be slow enough for the system to remain almost entirely in an energy eigenstate. The work done, say for example by moving a piston, involves a change in energy of both parts $A$ and $B$. Although the piston is part of system $A$, a flow of energy from $B$ to $A$ can also occur, and such a flow will contribute to the total amount of work done in changing $x$. This is familiar in the common thermodynamics example of the expansion of a gas under adiabatic conditions, or under constant temperature conditions. In the latter case, heat flows from a heat bath into the gas, contributing to the work done. Therefore the work done involves the total change in the energy of $A$ and $B$ although the piston is only attached to $A$.

Secondly, statistical mechanical entropy of system $A$, $S_A$, is defined as $S_A = \ln \Omega_A$, where $\Omega_A$ is the number of states in the energy window being considered. Then, as shown by Reif [18],
\[ \frac{\partial S_A}{\partial x} = - \frac{1}{T} \left( \frac{\partial H_A}{\partial x} \right)_A. \] (15)

The microcanonical average is being taken at an energy $E_A = \langle \psi | H_A | \psi \rangle$ for only subsystem $A$. Appendix B gives a simple derivation of this.

Then one writes the differential
\[ dS_A = \frac{\partial S_A}{\partial E_A} dE_A + \frac{\partial S_A}{\partial x} dx. \] (16)

Note from equations (13) and (15) that
\[ dS_A = \frac{1}{T} \left( dE_A - \frac{\partial E}{\partial x} dx \right). \] (17)

The last equality involves $dE_A + dW$, which is the usual definition of the total heat $dQ$ absorbed by $A$. Hence
\[ dS_A = \frac{dQ}{T}. \] (18)
Therefore the ensemble definition of the entropy is related to the flow of energy $dQ$ between subsystems $A$ and $B$ by the usual thermodynamic relation, equation (18). For thermodynamic purposes, the energy flow $dQ$ is completely equivalent to heat, yet it is seen for a system in an energy eigenstate. A change in an external parameter acting on one part of a system in an energy eigenstate will cause entropy to redistribute itself across subsystems.

It must be emphasized that a crucial step in this analysis is the assumption of energy eigenstate thermalization, for which, as mentioned above, there is both theoretical and numerical evidence [12, 13, 16].

Although the above does not show that there is an entropy associated with a complete system in an energy eigenstate, it shows that entropy changes of subsystems can be induced by a slowly varying external parameter. This does not prove that there exists a well-defined entropy for each subsystem in isolation, but shows that despite the trivial time dependence of an energy eigenstate, heat can flow internally between different parts of it. This is interesting in its own right but is only suggestive of the idea that the system as a whole has a nonzero thermodynamic entropy associated with it.

In the next section, we argue that there is a thermodynamic entropy associated with an energy eigenstate and it can be calculated by means of the entanglement entropy.

4. Analysis of the entanglement entropy

4.1. The model

As discussed earlier in section 1, we consider a system in an eigenstate energy $E$ and with $n_{\text{tot}}$ degrees of freedom. We subdivide it into two macroscopic systems, one $\phi$ and the other $\theta$ with $n$ and $m$ degrees of freedom, respectively. We will consider $n$ large but $m > n$. If both subsystems were uncoupled, we can diagonalize each of them into energy eigenstates forming a complete set of $|\phi_i\rangle$ and $|\theta_j\rangle$. The wave function for the complete system can then be written as

$$|\psi\rangle = \sum_{i,j} C_{ij} |\phi_i\rangle |\theta_j\rangle.$$  \hspace{1cm} (19)

The summation is over all states.

Consider the case where the coupling Hamiltonian $H_1$ between $m$ and $n$ is weak. Then to first order in perturbation theory an energy eigenstate of the uncoupled system $|\phi_0\rangle |\theta_0\rangle$ is altered by $H_1$ as follows

$$|\psi\rangle = \sum_{i,j} \frac{\langle \theta_j | H_1 | \phi_0 \rangle |\theta_0\rangle}{E_0 - E_{i,j}} |\phi_i\rangle |\theta_j\rangle.$$  \hspace{1cm} (20)

As we argued above, $\langle \theta_j | H_1 | \phi_0 \rangle |\theta_0\rangle$ will become exponentially small when the energy difference between the bra and ket states is much greater than $T$. Higher order terms in the perturbation series also have this property. Therefore applying a perturbation that couples $n$ and $m$ will only allow a coupling if their energies differ by a microscopic energy of order $T$.

Because coefficients $C_{ij}$ are identical to those in equation (20), the only ones that need be considered are those where the energy of state $|\phi_i\rangle |\theta_j\rangle$ is almost constant.

Although I expect the arguments here to hold more generally, one can make the model more precise by adopting an approach similar to that used in section 3. We choose the energy eigenvectors as a basis for $|\psi\rangle$ before coupling $H_1$ is turned on. Therefore, the energy in an
eigenstate $|\phi\rangle\langle\theta|$ is the sum of the energy of $\phi$ plus the energy of $\theta$. When the interaction $H_i$ is switched on, the effects of this coupling can be modeled, as was done in section 3, as a banded random matrix. In this case, $C_{ij}C_{kl}$, averaged over different realizations of $H_i$, are zero for $i \neq k$ or $j \neq l$.

The argument that we present now is analogous to the standard argument of energy exchange between two subsystems [1]. Out of states $|\phi_i\rangle\langle\theta_j|$ that will contribute to $|\psi\rangle$, there will be ones where the energy $e_\phi$ of subsystem $\theta$ is high and $e_\phi$ is low, and vice versa. Because the density of states of each subsystem increases extremely rapidly with energy, there will be a very sharp peak in the number of states that contribute as a function of $e_\phi$. This means that the two subsystems will be at the same ‘temperature’ and the standard deviation in energy of one subsystem $\Delta E \propto \sqrt{C_{nm}}/(n+m)T$, where $C$ is the specific heat per degree of freedom. This is much greater than the microscopic thermal energy $T$ but much less than the total energy of $|\phi\rangle$.

4.2. Entanglement entropy calculation

The density matrix of the $\phi_i$ in the $|\phi\rangle\langle\theta|$ basis, tracing over $\theta$ can be represented as

$$\rho_{ij} = \sum_k C_{ik}C_{jk}^*.$$  \hfill (21)

First we will examine the diagonal portion of this density matrix, $\rho_{ii}$. By completeness, $\text{tr}(\rho) = \langle\psi|\psi\rangle = 1$. By integrating over a subsystem $m$, $\rho_{ij}$ will be close to zero outside a window that depends on the size of $m$. To estimate the size of this window, we note that total energy of the isolated system is conserved. First consider $\rho_{ii}$ averaged over an ensemble of $C$’s (or random matrices)

$$\overline{\rho}_{ii} = \sum_{j=1}^M |C_{ij}|^2.$$  \hfill (22)

The number of states effectively contributing, $M$, is finite, because, as we just argued, conservation of energy and the very sharp peak in the density of states as a function of $e_\phi$ imply that only states of $\theta$ with an energy within a few windows of $\Delta E$ will contribute to this sum. Therefore $M \propto \Delta E \exp(ns(E/n_{\text{tot}}))$, $s$ being the microcanonical entropy per degree of freedom. In equation (22), we expect $|C_{ij}|^2$ to be a smooth function of the $j$’s in analogy to equation (10). Because $\sum_i \rho_{ii} = 1$, we can estimate the entropy as follows. The number of terms contributing to this sum is $N = \Delta EG(E)$, where $G(E)$ is the density of states of subsystem $\phi$ and is $\propto \exp(ns(E/n_{\text{tot}}))$. We take the terms in this window to be constant so that $\overline{\rho}_{ii} = 1/N$. To get our initial estimate, we will assume that all off-diagonal components are negligible (but we will do a better job below). Therefore this entropy estimate is then $-\sum_i \rho_{ii} \ln \rho_{ii}$, which is then $N(1/N) \ln(N)$. But $N \propto \sqrt{n} \exp(ns(E/n_{\text{tot}}))$. For large $N$, this becomes $nS(E/n_{\text{tot}}) + O(\ln n)$. For large $n$, this becomes precisely the entropy of the subsystem $\phi$.

This crude approximation to the density matrix gives the correct answer for the same reason that it works for many statistical mechanical calculations. Only the peak value of $\rho_{ii}$ matters after taking a logarithm. Therefore one could instead have taken a non-flat distribution for $\rho_{ii}$ and this would not have altered the dominant term. However, by pre-averaging $\rho$, we ignored fluctuations which will be sizable if $m$ is small. To estimate these, we expand $\rho_{ii} = \overline{\rho}_{ii} + \delta \rho_{ii}$.
Then we average to find the size of the fluctuations. Expanding ρ_{ii} ln ρ_{ii} in δρ_{ii} and averaging, the first-order terms vanish, leaving a correction δρ_{ii}^2/(2ρ_{ii}).

With uncorrelated C_{ij}'s, δρ_{ii}^2 = var(ρ_{ii}) ∼ M var(|C_{ij}|^2). We also expect that the C_{ij}'s will be close to Gaussian, which means that var(|C_{ij}|^2) ∝ |C_{ij}|^2. Because ρ_{ii} \sim 1/N, (|C_{ij}|^2) ∝ 1/(N M), which implies that δρ_{ii}^2 ∝ M var(|C_{ij}|^2). Therefore

\[
\sum_i \frac{δρ_{ii}^2}{(2ρ_{ii})} = N \frac{M(1/NM)^2}{1/N} = \frac{1}{M}. \tag{23}
\]

Therefore we expect that corrections to the diagonal elements of the density matrix will be exponentially small in the system size m.

We will now turn to a calculation of the contribution of the entanglement entropy due to off-diagonal matrix elements. We will first estimate the size of the off-diagonal portions of the density matrix, and to do this we will again assume, as with a random matrix model, that as above the C_{ij} have random phase and are uncorrelated. Averaging over random realizations of the C’s gives an estimate for the variance of ρ_{ij}. For i \neq j,

\[
|\rho_{ij}|^2 = \sum_{m,n} C_{im} C_{jm} C_{in} C_{jn} = \sum_n |C_{in}|^2 |C_{jn}|^2 \sim O \left( N \left( \frac{1}{NM} \right)^2 \right) = O \left( \frac{1}{N^2 M} \right). \tag{24}
\]

Because this is much smaller than the order of ρ ∼ O(1/N), it makes sense to treat the off-diagonal elements perturbatively.

We expand the density matrix

\[
ρ_{ij} = D_{ij} + ε_{ij}, \tag{25}
\]

where D_{ij} is the diagonal part of the density matrix and ε_{ij} is the remaining off-diagonal terms, with ε_{ii} = 0. The entropy is S(ρ) = -tr(ρ ln ρ).

We expand the entropy around ρ = D to second order in ε. This is calculated in appendix C and gives

\[
S_2(ρ) = \frac{1}{2} \sum_{nm} F(ρ_{nn}, ρ_{mm}) ρ_{nm}^2. \tag{26}
\]

The function F(x, y), defined in equation (C.13), is symmetric in its arguments and is peaked along the line x = y, where it has the value F(x, x) = 1/x. As x and y go to zero, the summand in equation (26) is well behaved as can be checked as follows.

By Schwartz’s inequality equation (21) implies

\[
ρ_{ij}^2 = \left( \sum_m C_{im} C_{jm} \right)^2 \leq ρ_{ii} ρ_{jj}. \tag{27}
\]

Therefore

\[
|F(ρ_{nn}, ρ_{mm}) Re(ε_{nm}^2)| \leq |F(ρ_{nn}, ρ_{mm}) ρ_{mn} ρ_{nn}|. \tag{28}
\]

And it is easily seen that the function F(x, y)x\,y is well behaved for small x and y.

Now we are in a position to estimate the order of the off-diagonal contribution S_2 to the total entanglement entropy S using equation (26). With N^2 terms in the sum, ρ_{nm}^2 estimated using equation (24), and F contributing O(\ln ρ_{ii}/ρ_{ii}) = O(\ln N/(1/N)) = O(N \ln N), this gives

\[
S_2 \sim N^2 N \ln N \left( \frac{1}{N^2 M} \right) \sim O(\ln N)N/M. \tag{29}
\]
The diagonal term, which is also the thermodynamic entropy, is \( \ln N \). Therefore, for \( N \ll M \), the off-diagonal contribution to the entropy is negligible and the entropy is given by the ensemble result. Also note that for a homogeneous system in order for \( S_2 \) to be small compared to the canonical result, one does not require \( n \ll m \). Because \( \ln(N/M) \propto n - m \) one instead requires that \( m - n \) is large. For a macroscopic system, \( m - n \) can be made very large, while \( (m - n)/m \) can be very small. This suggests that in the limit of large \( n \), the entanglement entropy will be equivalent to the canonical entropy for \( n/m < 1 \).

Because the entanglement entropy of \( \phi \) is identical \([2]\) to that of \( \theta \), for \( n/m > 1 \), the entropy obtained from the entanglement entropy becomes that of system \( \theta \).

5. Discussion

5.1. Is measurement responsible for zero entropy?

There are many definitions of the entropy, and it is often couched in terms of the lack of information about a system. Classically, the relationship between information and the system’s state is straightforward. If the microscopic state of a system is completely characterized, this means that we have all possible information about it. But a gas applies the same time-averaged pressure to a piston irrespective of the experimenter’s state of ignorance. The entropy used for thermodynamic purposes is not dependent on our knowledge of the system, so that derivatives of the entropy with respect to parameters such as volume via equation (15) give us experimentally measurable quantities such as the pressure. That is why, in this work, I have concentrated on understanding the thermodynamic entropy. This entropy is calculable through standard means, such as the canonical ensemble.

However, the situation becomes murkier when considering quantum mechanics. The process of obtaining a precise state involves measurement, which couples the system of interest to another system. This changes its state. Therefore the act of measuring a system’s energy precisely, so as to put it into an energy eigenstate, might then affect its thermodynamic entropy.

If a system starts out in some generic pure state with many different components in different energy eigenstates and one measures the energy precisely, this puts it into an energy eigenstate. One can construct an argument suggesting that contrary to the claims here, the entropy after such a measurement would be greatly affected. If the system starts out with an energy spread over some width, for example corresponding to the wavelength of a box size, it is the sum of an exponentially large number \( N \propto \exp(S) \) of energy eigenstates \( |e_i \rangle \) so that \( |\psi \rangle = \sum_i a_i |e_i \rangle \) with some coefficients \( a_i \). The entropy would come from the lack of knowledge of these coefficients. If the energy is measured to sufficient accuracy so as to put it into a single energy eigenstate, then this has reduced the number of coefficients in this sum down to one. The energy measurement outputs a number of great accuracy describable by a minimum of \( \log_2(N) \) bits. This is a large number that is extensive in the size of the system, \( n \). This much information being produced, and the collapse of the wave function to a single energy eigenstate, might give one reason to believe that the thermodynamic entropy has been reduced by an extensive amount.

However, there are two problems with this argument. Firstly, as we argued above for the classical regime, the act of the measurement process does not alter the thermodynamic entropy. If, indeed, it were true that a system in a pure state has zero thermodynamic entropy, then it would be impossible to extract heat from it. For example, placing it in contact with another system that is initially in its ground state, should then result in no flow of heat. This appears
to be incorrect. Secondly, for the entropy of the system to decrease, heat must flow into the measuring apparatus. But a measurement by itself does not necessarily cost any energy. As shown by Bennett [19], it does not cost energy to find the state of a two-state system, if this is done sufficiently slowly. If the apparatus was originally in a known standard state, it will find itself in a different state after the measurement process, and that state will depend on the outcome of the measurement. In order for further measurements to take place, the apparatus needs to be reset, which means that the phase space of the measurement apparatus must be contracted, which will cost an energy $k_B T/2$.

The above arguments suggest that a system in a pure state should have a positive entropy in accord with the thermodynamic definition. A measurement of a system over an extremely long period of time will not collapse the entropy to zero.

5.2. Entanglement entropy at finite temperature

I have calculated the entanglement entropy of an energy eigenstate with an energy equivalent to a system at finite temperature, to leading order in the size of the system. For notational simplicity, I have occasionally assumed that the system is homogeneous; however, the results should apply for non-homogeneous systems. The complete entropy is obtained by dividing the system in several ways into unequal sized subsystems and calculating the sum of their respective entanglement entropies.

There will be corrections to this prescription that become small for large system size. Exact results for zero temperature systems is an indication of the presence of sub-extensive terms that have many interesting applications [7, 8]. The methods used here do not easily give non-extensive corrections and consequently do not give these zero temperature results.

The result found here for large ‘ergodic’ systems is surprising, in that the entanglement entropy is linear in the number of degrees of freedom for the smaller subsystem. This works with exponentially small corrections up to the point when the two subsystems are of almost equal size. It is surprising that the crossover of the entanglement entropy at this point is so sharp.

The result that the entanglement entropy of a finite temperature system is equal to the thermodynamic entropy can be shown rigorously to be true in special cases [9]–[11]. This was shown to be the case for 1 + 1-dimensional conformal field theories in a finite temperature mixed state ensemble, where the system of interest is connected to an infinite system. It is not surprising that in this limit, one obtains the usual entropy as a canonical ensemble has been used that acts, in effect, as a heat bath. In this paper, we analyzed the case where the system is in an energy eigenstate and reached the same conclusion concerning the entanglement entropy. In this case, there is no heat bath, only the coupling of the subsystem of interest to the rest of the system. It is not obvious that such a coupling should be enough to result in the answer one obtains for a mixed state. The model that we used was similar to that of the previous work [12], and assumes that the coupling between the two parts of the system $\phi$ and $\theta$ is sufficiently chaotic to be describable by random matrices. This is certainly an approximation and for short-range forces, the interactions between the two should be taking place only on the interface between the two subsystems. However, I conjecture that the result is robust enough to apply to such cases. Numerical work should, in principle, be able to test the arguments presented here.
5.3. Thermodynamics of pure states

I also looked at the effects of external forces that are slowly applied to an energy eigenstate in section 3. A many body energy eigenstate responds to external perturbations through the flow of heat obeying the usual relationship between the change in heat and the change in entropy. The result only shows that there is a flow of heat between two subsystems, A and B. It does not show that a complete energy eigenstate can be induced to have a change in its entropy due to the flow of energy. In order to do so, the coupling between systems A and B would have to be turned off slowly. This is a delicate issue for two reasons. The first is that energy eigenstate thermalization will not work when the coupling between A and B becomes too small. Secondly, it can easily be seen that if the decoupling is adiabatic, then a macroscopic amount of energy will, in general, flow between the two subsystems. Thus, one cannot easily separate the subsystems without drastically altering them macroscopically.

To find an adequate way of separating the subsystems, one must make further assumptions about the nature of the system, by assuming that the interactions are local so that there is a maximum speed of propagation of energy through it. Thus, for an extremely large system, there should be a regime where (a) the interaction between A and B can be switched off slowly enough so that the spread in energy of the wave function stays sub-extensive and (b) the switching is rapid enough so that the effect of the disturbance at the interface between A and B only allows energy to propagate a negligible distance in comparison with the system size and therefore the average energy density of both subsystems remains almost unchanged. If the complete system starts in an energy eigenstate, and the external parameter \( x \) is then varied adiabatically for \( A \), this, as was shown, exchanges heat between A and B. At this point the subsystems can be separated so as to satisfy criteria (a) and (b). The final subsystems will no longer be in energy eigenstates but still be in pure states with energy uncertainties that are sub-extensive. The value of \( x \) can then be brought back adiabatically to its initial value. This allows for the determination of relative entropies by varying the final value of \( x \) before separation, similar to how entropy is determined by thermodynamic means.

Although the procedure does not define entropy for energy eigenstates, it gives a prescription for pure states, which is interesting, because such states have a zero von Neumann entropy.

If it turns out that the entanglement entropy construction described here is not the correct measure of the thermodynamic entropy for energy eigenstates, the above argument makes it likely that there is another prescription for it involving solely the wave function.

5.4. Related work

There has been a number of recent papers considering the relationship between entropy and quantum mechanics [20]–[23]. They differ in several respects. Gemmer et al [20] consider two coupled subsystems, one acting as the environment, and analyze the von Neumann entropy of one of the subsystems of interest. In the case analyzed in the present paper, the complete system is in an energy eigenstate and their analysis is inapplicable. The work of Popescu et al [21] does not involve time evolution and involves a Hamiltonian only to the extent that it defines ‘grand canonical’ restrictions. In a related and more recent work, Linden et al [22] studied time evolution and showed that, for long times, correlations and entanglement of the energy eigenstates determine the statistical mechanics properties of a finite temperature system.
The approach taken in the present work is rather different and addresses different problems. Here we want to consider a single isolated system and study how individual states give rise to thermodynamic properties, such as the entropy. This means that time averaging, or energy eigenstates, must be considered in order to obtain the expectation values of typical observables. This has an analogy with classical statistical mechanics, where entropy is defined using the fundamental hypothesis of Boltzmann [1], thus requiring averages over time in order to obtain a good estimate of phase-space volume and of time averages. Because of the lack of an ensemble, the nature of the Hamiltonian is very important (in contrast to recent work by Reimann [23]) and is required to obtain the correct correspondence with statistical mechanics. As discussed in an earlier work [12], a quantum integrable system, starting off far from equilibrium, will not give time averages in accord with the microcanonical ensemble. On the other hand, if instead one would like to obtain instantaneous properties, one cannot utilize time averaging, and such problems are facilitated by considering an ensemble of baths [22] and a subsystem of interest coupled to them.

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Appendix A. Range of potential matrix elements

In this appendix, we justify in more detail the cut-off on the random matrix used in calculations. We are interested in determining how $\langle E | V | E' \rangle$ varies with increasing $E - E'$. The quantity we wish to compute is $\langle \langle E | V | E' \rangle \rangle_{E, E'}$. Here the second set of brackets denotes a microcanonical average over both $E$ and $E'$. $V$ is taken to be of the form (3), and we consider a system of identical particles that are either fermions or bosons. Label the eigenstates of a single particle by $i$. The energy in that state is labeled $e_i$, the total number of particles in state $i$ is $n_i$ and $n_i \leq 1$ for the case of fermions. In the second quantized notation, the total wave function can be written as

$$|E\rangle = \prod_i a_i^{n_i} |0\rangle,$$

where $|0\rangle$ is the ground state. The potential $V$ can also be written in the second quantized form as

$$V = \sum_{j,k,l,m} V_{jklm} a_j^\dagger a_k^\dagger a_l a_m,$$

where

$$V_{jklm} = \int \psi_j^*(r) \psi_k^*(r') V(r - r') \psi_l(r) \psi_m(r') \, dr \, dr',$$

and in this case, $\psi_j$ denotes a plane wave with wavevector indexed by $j$. Thus, the quantity we wish to compute is

$$\langle \langle E | V | E' \rangle \rangle_{E, E'} = \frac{1}{n(E) n(E')} \sum_{n,s} \sum_{n',s'} \delta \left( E - \sum_i n_i e_i \right) \delta \left( E' - \sum_i n'_i e'_i \right) \langle E | V | E' \rangle,$$
where \( n(E) \) is the appropriate normalization. In the above, \( \sum_{n_i} \) means the sum over all possible combinations of \( n_i \)'s with the constraint \( \sum_i n_i = n \). Writing the above equation in the second quantized form and taking the inner products gives

\[
\langle \langle E | V | E' \rangle \rangle_{E,E'} = \frac{1}{n(E)n(E')} \sum_{j,k,l,m} \sum_{n_{i,j},n'_{i,m}} \delta \left( E - \sum_i n_i e_i \right) \sqrt{n_j n_k n'_l n'_m} \\
\times \delta (E - E' - (e_j + e_k - e_l - e_m)) V_{jklm} \\
= \frac{1}{n(E')} \sum_{j,k,l,m} \sum_{n_{i,j},n'_{i,m}} \langle \delta (E - E' - (e_j + e_k - e_l - e_m)) \rangle \sqrt{n_j n_k n'_l n'_m} V_{jklm} E, \tag{A.5}
\]

where the last bracket denotes a microcanonical average at energy \( E \). As long as \( |E - E'| \ll E \), and \( n \) is large, the microcanonical average here can be replaced by a canonical average at the appropriate temperature \( T \) as given in (2.4) where

\[
S = \ln \left( \sum_{n_{i,j}} \delta \left( E - \sum_i n_i e_i \right) \right). \tag{A.6}
\]

If we consider potentials \( V(r) \) which have a Fourier transform that is bounded, then so is \( V_{jklm} \) as the single particle eigenstates are plane waves. We can therefore bound the above equation by

\[
\frac{1}{n(E')} \sum_{j,k,l,m} \sum_{n_{i,j},n'_{i,m}} \langle \delta (E - E' - (e_j + e_k - e_l - e_m)) \rangle \sqrt{n_j n_k n'_l n'_m} E. \tag{A.7}
\]

Now consider what happens for \( E - E' \gg T \). In this limit, it is straightforward to substitute in the appropriate Bose or Fermi distributions for each \( n_i \) and perform the summations, but the asymptotic result can be seen by the following argument. The above average only has contributions to it when \( e_j + e_k = e_l + e_m + E - E' \). If \( E' \) is kept fixed and \( E \) is increased, then the minimum energy needed to obtain a contribution occurs when \( e_l = e_m = 0 \), so that \( e_j + e_k = E - E' \). (Here we are setting the ground state energies equal to zero.) As \( E \) is increased the weight of having such a configuration is given by the appropriate Bose or Fermi distributions which asymptotically give a weight of \( \exp(-e_j - e_k) = \exp(-(E - E')/T) \). Considering larger \( e_j \) and \( e_m \) does not change the weight of the above exponential dependence, but just the overall pre-factor.

**Appendix B. Relation between entropy and forces**

Here, we present a derivation of equation (15) that is shorter than other treatments that the author is aware of.

Consider the integral of the density of states

\[
I(E) = \int_{-\infty}^{E} e^{S(E')} \, dE' = \int_{-\infty}^{E} \text{tr} \, \delta (E - H) = \text{tr} \, \theta (E - H), \tag{B.1}
\]

where the last equality uses the Heaviside function \( \theta \).
Because the entropy is rapidly increasing for a system with a large number of degrees of freedom \( n \), we expand it about \( E \), in the exponent of the above integrand,

\[
S(E') = S(E) + \frac{\partial S}{\partial E} (E' - E) + \cdots = S(E) + \frac{1}{T} (E' - E) + \cdots.
\]

So that for large \( n \),

\[
I(E) = \int_{-\infty}^{E} e^{S(E')} dE' = Te^{S}(E).
\]

Now consider a Hamiltonian that depends on a parameter \( x \),

\[
\frac{\partial \ln I(E)}{\partial x} = -\frac{\text{tr}(\delta(E - H) \frac{\partial H}{\partial x})}{Te^{S}} = -\frac{1}{T} \left( \frac{\partial H}{\partial x} \right).
\]

One can relate the left-hand side to the entropy as follows:

\[
\frac{\partial \ln I(E)}{\partial x} = \frac{\partial S(E)}{\partial x} + \frac{\partial T}{\partial x},
\]

which for large \( n \) becomes \( \partial S/\partial x \), giving equation (15).

**Appendix C. Calculation of the off-diagonal component of entropy**

We wish to calculate the effects of small off-diagonal elements of the density matrix on the entropy \( S(\rho) = -\text{tr}(\rho \ln \rho) \), by writing \( \rho_{ij} = D_{ij} + \epsilon_{ij} \).

To simplify the expansion, first define \( f(x) = -x \ln(x) \). There is no power series expansion of this about \( x = 0 \), but we can regularize it to allow such an expansion, for example \( f(r) = f(x + \delta) \). We will see that at the end, we can take the limit \( \delta \to 0 \) without difficulty. With a regularized \( f \), we can expand it as

\[
f(x) = \sum_{n=0}^{\infty} a_n x^n.
\]

The \( \epsilon^0 \) term yields \( S_0 = \text{tr}(f(D)) \), as expected. The \( \epsilon^1 \) term is zero because \( \text{tr}(D^{i} \epsilon) = \sum_i D_{ii}^{i} \epsilon_{ii} = 0 \).

To obtain the \( \epsilon^2 \) contribution, we note that \( \epsilon \) and \( D \) are, in general, non-commuting, and therefore we must preserve matrix ordering when expanding \( (D + \epsilon)^n \). Denoting terms second order in \( \epsilon \) by \( S_2 \), we have

\[
S_2(\rho) = \text{tr} \left( \sum_{n=0}^{\infty} a_n (D + \epsilon)^n \right) = \sum_{n=0}^{\infty} a_n (D + \epsilon)^n.
\]

However, because for two matrices \( A \) and \( B \), \( \text{tr}(AB) = \text{tr}(BA) \), we can reorder a given term so that the final matrix is always \( \epsilon \), so that the summand becomes \( D^i \epsilon D^j \epsilon \). This reordering generates \( i + k + 1 \) such terms. So, simplifying the indices gives

\[
S_2(\rho) = \text{tr} \left( \sum_{i,j=0}^{\infty} (i + 1) a_{i+j+2} D^i \epsilon D^j \epsilon \right).
\]
We now commute the trace with the summations and perform it first. It has the general form
\[ \text{tr}(A \epsilon B) \] with \( A \) and \( B \) diagonal and real. In this case, this is easily seen to be
\[ \sum_{n,m} A_{nn} B_{mm} \epsilon_{nm}^2. \] (C.5)

Switching indices \( m \) and \( n \) and using the fact that, in the situation discussed here, \( \epsilon \) is Hermitian and \( A_{nn} B_{mm} = A_{mm} B_{nn} \) yields
\[ \text{tr}(A \epsilon B) = \sum_{n,m} A_{nn} B_{mm} \epsilon_{nm}^2, \] (C.6)
where \( \epsilon_{nm}^2 = \text{Re}(\epsilon_{nm}^2) \).

Using this in equation (C.4) gives
\[ S_2(\rho) = \sum_{n,m=0}^{\infty} \left( \sum_{i,j=0}^{\infty} (i+1) a_{i+j+2} D_{nn}^i D_{mm}^j \right) \epsilon_{nm}^2. \] (C.7)

Because \( \epsilon \) is symmetric, the indices \( m \) and \( n \) can be exchanged, and so after switching the dummy variables \( i \) and \( j \), we can add this relabeled expression to the above, giving
\[ S_2(\rho) = \sum_{n,m=0}^{\infty} \left( \sum_{i,j=0}^{\infty} (i+j+2) a_{i+j+2} D_{nn}^i D_{mm}^j \right) \epsilon_{nm}^2. \] (C.8)

We can write the term in parentheses as \( F(D_{nn}, D_{mm}) \) where
\[ F(x, y) = \sum_{i,j=0}^{\infty} (i+j+2) a_{i+j+2} x^i y^j \] (C.9)
and we wish to find a closed form expression for this in terms of \( f_r(x) \), which has the \( a_n \)'s coefficients as its power series expansion. To do this, we group all terms according to the value of \( n \equiv i + j \). Therefore
\[ F(x, y) = \sum_{n=0}^{\infty} (n+2) a_{n+2} (x^n + x^{n-1} y + \cdots + x y^{n-1} + y^n) \]
\[ = \sum_{n=0}^{\infty} (n+2) a_{n+2} \frac{(x^{n+1} - y^{n+1})}{x - y}. \] (C.10)

This can be further simplified by noting that
\[ \sum_{n=0}^{\infty} (n+2) a_{n+2} x^{n+1} = \sum_{l=2}^{\infty} l a_l x^{l-1} = f'_r(x) - f'_r(0), \] (C.11)
where the prime denotes the first derivative. Substituting this into equation (C.10) gives
\[ F(x, y) = \frac{f'_r(x) - f'_r(y)}{x - y}. \] (C.12)

Note that because of the cancellation of \( f'_r(0) \), we can now take the limit as \( \delta \to 0 \) and use \( f = -x \ln x \) instead. This yields
\[ F(x, y) = \frac{\ln x - \ln y}{x - y}. \] (C.13)
Summarizing, we have shown that the second-order correction to the entropy due to off-diagonal components of the density matrix $\epsilon$ is

$$S_2(\rho) = \frac{1}{2} \sum_{n,m=0}^{\infty} F(\rho_{nn}, \rho_{mm}) \Re(\epsilon_{nm}^2).$$  \hspace{1cm} (C.14)

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