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Quantum heat engines, the second law and Maxwell's daemon

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Abstract. We introduce a class of quantum heat engines which consists of two-energy-eigenstate systems, the simplest of quantum mechanical systems, undergoing quantum adiabatic processes and energy exchanges with heat baths, respectively, at different stages of a cycle. Armed with this class of heat engines and some interpretation of heat transferred and work performed at the quantum level, we are able to clarify some important aspects of the second law of thermodynamics. In particular, it is not sufficient to have the heat source hotter than the sink, but there must be a minimum temperature difference between the hotter source and the cooler sink before any work can be extracted through the engines. The size of this minimum temperature difference is dictated by that of the energy gaps of the quantum engines involved. Our new quantum heat engines also offer a practical way, as an alternative to Szilard's engine, to physically realise Maxwell's daemon. Inspired and motivated by the Rabi oscillations, we further introduce some modifications to the quantum heat engines with single-mode cavities in order to, while respecting the second law, extract more work from the heat baths than is otherwise possible in thermal equilibria. Some of the results above are also generalisable to quantum heat engines of an infinite number of energy levels including 1-D simple harmonic oscillators and 1-D infinite square wells, or even special cases of continuous spectra.

PACS. 05.90.+m Other topics in statistical physics, thermodynamics, and nonlinear dynamical systems – 05.70.-a Thermodynamics

1 Introduction

The second law has started out as a "no-go" statement against a certain class of perpetual machines but is now a pillar of modern physics, supported by experimental evidence without exception so far. While the first law of thermodynamics is a statement of quantity about energy conservation, the second law is a statement of quality about what kinds of energy transformations are and are not allowed. There are several classical statements of the second law [1,2]:

- **Kelvin-Planck:** No process is possible whose *sole* result is the absorption of heat from a reservoir and the conversion of this heat into work;
- **Clausius:** No process is possible whose *sole* result is the transfer of heat from a cooler to a hotter body;
- **Entropy Maximum Postulate:** The entropy of a closed system never decreases in any process.

The first two statements above can be shown to be equivalent by the introduction of intermediate heat engines. And the last postulate requires the introduction of entropy which is a function of extensive parameters of a composite system, defined for all equilibrium states and having certain properties.

Entropy of a composite system in a macro-state can be linked, in statistical physics, to the statistics of the many micro-states that correspond to the same macro-state. In order to satisfy the statistical nature of entropy and to derive the principle of increasing entropy, several fundamental assumptions are required [3]:

- the composite system has a large number of components (atoms, molecules, etc.);
- these components can be divided into a small number of classes of indistinguishable components (in fact, were every molecule of a gas assumed to be different from each other then statistical physics would become fairly simple but useless as it would not be able to account for the non-decreasing flow of entropy);
- Boltzmann's fundamental hypothesis [4]: all micro-states are equally probable. This is termed as *elementary disorder* by Planck and has been generalised to the quantum domain as the hypotheses of equal a priori probabilities and random a priori phases for the quantum states of a system [5]. All of these can be subsumed by the (somewhat stronger) *ergodic*

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hypothesis [4] which postulates that the dynamical time average is equal to the ensemble average (of appropriate ensembles), except for a number of exceptional initial conditions of relatively vanishing importance.

No matter how reasonable the last assumption may be, it should be pointed out that those hypotheses are not a part of but are extra to the first principles of quantum mechanics.

The second law was indeed the motivation and the philosophical reason for Max Planck to introduce the concept of energy quanta in his solution for the puzzle of black-body radiation [3]. His line of reasoning can be rephrased as follows: the second law is about irreversibility in nature; irreversibility does nothing but defines a preference of the more probable over the less probable; and the probability assignment for physical states (in order to have the more and the less probables) requires those states to belong to a *distinguishable* variety of possibilities. This led Planck to the conclusion that the *atomic hypothesis* must be necessary. And the rest was history; the concept of quanta was then born as the states of discrete homogeneous elements. In that context, the study of heat engines in the quantum domain in relation to the second law is a contribution to a completion of the circle that was started at the beginning of the last century.

Present technology now allows for the probing and/or realisation of quantum mechanical systems of mesoscopic and even macroscopic sizes (like those of superconductors, Bose-Einstein condensates, etc.) which can also be restricted to a relatively small number of energy states. It is thus important to study these quantum systems directly in relation to the second law. Our study, started with [6] and further expanded in this paper, is part of a growing body of investigations into quantum heat engines [7–16]. Explicitly, the only principles we will need are those of the Schrödinger equation, the Born probability interpretation of the wavefunctions and the von Neumann measurement postulate [17]. In particular, we will not exclude, but will make full use of, any exceptional initial conditions, as long as they are realisable physically. However, without a better understanding of the emergence of classicality from quantum mechanics, we will have to assume the thermal equilibrium Gibbs distributions *for the heat baths* that are coupled to the quantum systems. This assumption is related to the fundamental assumptions mentioned above and is extra to those of quantum mechanics. Even though we do not impose this extra assumption on the quantum mechanical systems, the steady-state distributions *for the systems* will eventually reach the Gibbs distributions in time because of the coupling with the heat baths, see equation (14) below.

In order to introduce a class of heat engines operating entirely in the framework of quantum mechanics, we will need a quantum interpretation of the transfer of heat and performance of work in the next section. This interpretation is also necessary for a review of the second law and for a possible realisation, as an alternative to Szilard's engine, of Maxwell's daemon in Sections 3 and 4. The quantum heat engines are then considered next both in thermal equilibrium and also in thermal non-steady states, in Sections 5 and 6. We find from these quantum considerations that even though the second law is not violated in a broad sense, it needs some refinements and clarifications. We also demonstrate that more work can be extracted by the engines in non-steady states than otherwise is possible in thermal equilibrium, Section 7. Section 8 provides an explicit numerical illustration of such capability. We then discuss Maxwell's daemon further in Section 9 as the reason behind any violation of the second law were we ever able to control the quantum phases of the heat baths. Sections 10 and 11 contain some generalised results for quantum heat engines with simple harmonic oscillators and infinite square wells, respectively, all in one dimension. These results are indeed universal for certain class of quantum systems having continuous spectra. Finally, we end the paper with some concluding remarks in the final Section 12.

2 Quantum identifications of heat exchanged and work performed

The expectation value of the measured energy of a quantum system with discrete energy levels is

$$U = \langle E \rangle = \sum_i p_i \, E_i, \tag{1}$$

in which E_i are the energy levels and p_i are the corresponding occupation probabilities. Infinitesimally,

$$dU = \sum_i \{E_i \, dp_i + p_i \, dE_i\}, \tag{2}$$

from which we make the following identifications for infinitesimal heat transferred $đQ$ and work done $đW$

$$đQ := \sum_i E_i \, dp_i, \quad đW := \sum_i p_i \, dE_i. \tag{3}$$

Mathematically speaking, these are not total differentials but are path dependent. These expressions interpret heat transferred to or from a quantum system as the change in the occupation probabilities but not in the change of the energy eigenvalues themselves; and work done on or by a quantum system as a redistribution of the energy eigenvalues but not of the occupation probabilities of each energy level. Together with these identifications, equation (2) can be seen as just an expression of the first law of thermodynamics, $dU = đQ + đW$.

The above link between the infinitesimal heat transferred to the infinitesimal change of occupation probabilities is in accord with, or at least is not in contradiction to, the thermodynamic link between heat and entropy, $đQ = T \, dS$, in combination with the statistical physical link between entropy and probabilities, $S = -k \sum_i p_i \ln p_i$. On the other hand, expression (3) linking work performed to the change in energy levels agrees with the fact that work

done on or by a system can only be performed through a change in the generalised coordinates of the system, which in turn gives rise to a change in the distribution of the energy levels [18].

Starting, on the other hand, with the general expression for the energy average in terms of the density operator $\rho(t)$ and the time-dependent Hamiltonian $H(t)$,

$$U(t) = \mathrm{tr}\left[\rho(t)H(t)\right],$$

and its temporal derivative

$$\partial_t U(t) = \mathrm{tr}\left[\partial_t\rho(t)H(t)\right] + \mathrm{tr}\left[\rho(t)\partial_t H(t)\right],$$

we can otherwise identify the first term on the rhs as the rate of heat transferred, and the second the rate of work performed. This identification reduces to that in (3) above if we assume that, as is the case considered in this paper, when dealing with thermodynamical work, a concept which involves some energy coupling with a classical environment, the density operator becomes diagonal in the energy basis. This is the usual assumption of standard Quantum Mechanics for the emergence of classicality via measurement and/or decoherence.

3 A class of quantum heat engines

The quantum heat engines considered herein are just two-energy-level quantum systems, the simplest of quantum mechanical systems, operated in a cyclic fashion described below. (They are the quantum analogue of the classical Otto engines and are readily extendable to systems of many discrete energy levels.) They could perhaps be realised with coherent macroscopic quantum systems like, for instance, a Bose-Einstein condensate confined to the bottom two energy levels of a trapping potential. The exact cyclicity will be enforced to ensure that upon completing each cycle all the output products of the engines are clearly displayed without any hidden effect.

A cycle of the quantum heat engine consists of four stages:

- *Stage 1:* the system has some probability to be in the lower state *prior* to some kind of contact (whose nature will be discussed later on) with a heat bath at temperature T_1. After some time interval, there is a probability that the system receives some energy from the heat bath to jump up an energy gap of Δ_1 to be in the upper state. According to the interpretation of the last section, only heat is transferred in this stage to yield a change in the occupation probabilities, and no work done as there is no change in the values of the energy levels. This stage is depicted on the left hand side of Figure 1.
- *Stage 2:* the system is then isolated from the heat bath and undergoes a quantum adiabatic expansion, whose net result is to reduce the energy gap from Δ_1 to a smaller value Δ_2. In this stage, provided the expansion rate is sufficiently slow according to the quantum adiabatic theorem [19], the occupation probabilities for the two states remain unchanged. The system may perform an amount of work. This is depicted as the upper branch of Figure 1 running from left to right. Note that there is no change in probability so there is no heat transferred; that is, the amount of work performed by the system is maximal as all available energy is converted to work (see [20], for example, for a general proof and some further discussion). We also mention here that a quantum adiabatic process implies a thermodynamical adiabatic process, but not the other way around in general[1].
- *Stage 3:* the system is next brought into some kind of contact with another heat bath at temperature T_2 for some time. There is a probability that it releases some energy to the bath to jump down the gap Δ_2 to be in the lower state. This is depicted on the right hand side of Figure 1. Some heat is thus transferred but no work is performed in this stage.
- *Stage 4:* the system is removed from the heat bath and undergoes a quantum adiabatic contraction, whose net result is to increase the energy gap from Δ_2 back to

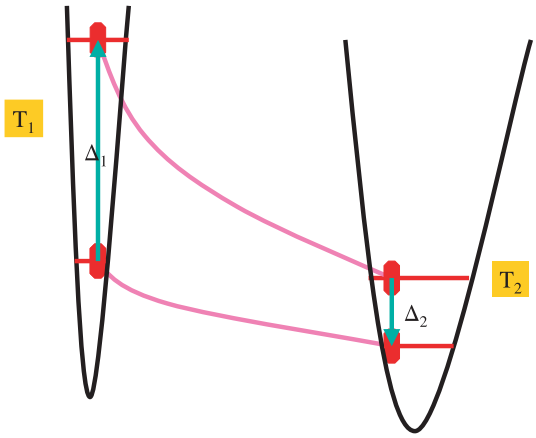

Fig. 1. On the left hand side, a two-state quantum system in the lower state comes into contact with a heat bath at temperature T_1 for some time until it absorbs an amount of energy Δ_1 to jump into the upper state. Next in the passage to the right hand side, the system undergoes a quantum adiabatic process, remaining in the upper state, and performs work on the relaxing potential wall. On the right hand side, the system comes into contact with another heat bath at temperature T_2 for some time until it releases an amount of energy Δ_2 to jump back to the lower state. In the final passage to the left hand side to complete a cycle of the heat engine, the system undergoes another quantum adiabatic process in which it remains in the lower state and work is done on the system by the compressing potential wall.

[1] The reverse is not in general applicable if the system consists of many quantum subsystems and if these are considered separately. Thermodynamical adiabaticity only means that the system as a whole has no heat exchange with the environment, but heat could still be exchanged internally between the quantum subsystems (resulting in some change in the occupational probabilities of the energy levels of the subsystems) due to some intra-couplings among themselves, such as collisions.

the previously larger value Δ_1. This is depicted as the lower branch of Figure 1 running from right back to left. In this stage an amount of work is done on the system, and this is the minimal required work as there is no energy wasted in the form of heat transferred to the system.

Ideal quantum adiabatic processes are employed here because they yield, on the one hand, the maximum amount of work performable *by* the systems in stage 2 (as the transition probabilities to the lower state in that stage can be made vanishingly small according to the quantum adiabatic theorem), but yield the minimum amount of work performable *on* the systems (by some external agents) in stage 4, on the other hand. In each cycle the amount of work done *by* the system is $(\Delta_1 - \Delta_2)$, which is also the net amount of heat it absorbs. Note that we need not and have not assigned any temperature to the quantum system; all the temperatures are properties of the heat baths, which in turn are assumed to be in the Gibbs state.

However, in the operation above, the absorption and release of energy in stages 1 and 3 occur neither definitely nor deterministically. Quantum mechanics tells us that they can only happen probabilistically; and the probabilities that such transitions take place depend on the details of the interactions with and some intrinsic properties (namely, the temperatures) of the heat baths.

Let $p_u^{(1,2)}$ be the probabilities for the system to be in the upper level at the beginning of stages 2 and 4, respectively. The net work done by our quantum heat engines in the two quantum adiabatic passages in stages 2 and 4 is

$$\begin{aligned} \Delta W &= \left(\int_{\text{left} \to \text{right}} + \int_{\text{right} \to \text{left}} \right) \sum_i p_i \, dE_i, \\ &= \left(p_u^{(1)} - p_u^{(2)} \right) (\Delta_2 - \Delta_1) \,. \end{aligned} \tag{4}$$

We will make full use of this simple expression in the sections below.

By the weak law of large numbers, probability reflects the relative occurrence frequency of an event in a large number of repetitions. In the case of thermal equilibrium with only one single heat bath ($T_1 = T_2$), even with a small probability $\tilde{p}_u^{(1)}(1-\tilde{p}_u^{(2)})$ the system could be in the upper level in stage 2 *and* in the lower level in stage 4, where $\tilde{p}$ is the thermal equilibrium probabilities in (5) below. The probability, however, diminishes exponentially for n_c consecutive cycles, $(\tilde{p}_u^{(1)}(1-\tilde{p}_u^{(2)}))^{n_c}$, in all of which the system would perform net work on the environment. As a result, there *are* certain cycles *whose* sole *result is the absorption of heat from a reservoir and the conversion of this heat into work, of the amount* $(\Delta_1 - \Delta_2)$!

This amounts to a violation of the Kelvin-Planck statement of the second law due to the explicit probabilistic nature of quantum mechanical processes. This violation of classical statements for the second law, however, occurs only randomly, with some vanishingly small probability *in the longer term*, and thus is not controllable — neither harnessible nor exploitable.

This may seem non-surprising given the statistical nature of the second law, but it is somewhat different from the usual scenario of violation of the second law by statistical fluctuations in the bulk. One example of this latter scenario is the instantaneous concentration of all the gas molecules in a big room into one of its corners. Mathematically, this configuration is permissible due to the existence of the Poincaré cycles in mechanics, but statistical physics effectively rules this out (gives it a vanishing probability) by invoking extra assumptions and hypotheses as mentioned in Section 1. The scenario with our quantum heat engines is different in that it only involves a single (macro) quantum system with physically realisable quantum mechanical probabilities, and without any extra hypothesis. The subtle difference between the two cases is in the time average for a single system, on the one hand, and the bulk average, on the other, for systems having many subcomponents. Further discussion on some difference between quantum and classical fluctuations of work can be found in [21].

4 A realisation of Maxwell's daemon

However, there exists a sure way to *always* extract work, to the amount of $(\Delta_1 - \Delta_2)$, in each completable "cycle" described in Section 3. In order to eliminate the probabilistic uncertainty in the thermalising contacts with heat baths,

- we prepare the system to be in the lower state prior to stage 1;
- we perform an energy measurement after stage 1 and then only let the engine continue to stage 2 subject to the condition that the measurement result confirms that the system is in the upper state; if this is not the case, we repeat this step;
- we next perform another measurement after stage 3 and then only let the engine continue to stage 4 subject to the condition that the measurement result confirms that the system is in the lower state; if this is not the case, we repeat this step.

All the measurements above are to ensure $p_u^{(1)} = 1$ and $p_u^{(2)} = 0$, *irrespective of the heat bath temperatures*, and thus to be *always* able to derive maximum work according to (4). That is, all this can be carried out *even for the case* $T_1 \leq T_2$ to extract, always and in a controllable manner, some work which would have been otherwise prohibited by the second law.

This apparent violation of the second law is analogous to that of Szilard's one-atom engine and is nothing but the result of an act of Maxwell's daemon [22]. Indeed, the condition of strict cyclicity of each engine's cycle is broken here. After each cycle the measurement apparatus, being a Maxwell's daemon, has already registered the conditioning results which are needed to determine the next steps of the engine's operation. In this way, there are extra effects and changes to the register/memory of the apparatus, even if we assume that the quantum measurement

steps themselves cost no energy and leave no net effect anywhere else. To remove these remnants in order to restore the strict cyclicity, we would need to bring the register back to its initial condition by erasing any information obtained in the measurements in each of the cycles, either by resetting its bits or by thermalising the register with some heat bath. Either way, extra effects are inevitable, namely an amount of heat of at least $kT\ln 2$ will be released per bit erased. This is the Landauer principle which saves the second law. More extensive discussions and debates on these issues can be found in the literature [22], and in particular in the quantum version of Szilard's engine by Zurek [7]. Lloyd in [23] has analysed carefully and in detailed the Landauer principle behind the working of Maxwell's daemon entirely in the framework of quantum mechanics. Maxwell's daemon has also been discussed [24] in the context of quantum error correction in quantum computation.

Our quantum heat engines could thus provide, in a different way to Szilard's engine, a feasible and quantum mechanical way to realise Maxwell's daemon.

5 Thermal steady states

We have pointed out in Section 3 that there are random instances where our quantum heat engines can extract heat from a single heat bath and totally turn that into work or, equivalently, can transfer heat from a cold to a hot source (and may also do some work at the same time). Nonetheless, on the long-time average, there is no violation of the second law.

If the system is allowed to thermalise with the heat baths in stages 1 and 3, the thermal equilibrium probabilities for the two energy levels only depend on the relevant temperatures and the energy gaps, but not on the initial states when the system is brought into contact with the heat bath, see (14) below. More explicitly, the probability $\tilde{p}_u^{(1)}$ to have the system *in the upper state* at the end of stage 1 after being thermalised with the heat bath at temperature T_1, and $\tilde{p}_u^{(2)}$ at the end of stage 3 after being thermalised with the heat bath at temperature T_2, respectively, are

$$\tilde{p}_u^{(i)} = 1/\left(1+\exp\{\Delta_i/kT_i\}\right),\ \text{for } i=1,2. \tag{5}$$

These probabilities are definitely *non-zero* and bounded by 0.5. From which, the work derived from (4) is

$$\Delta W_{\rm th} = \left(\tilde{p}_u^{(1)} - \tilde{p}_u^{(2)}\right)(\Delta_2 - \Delta_1). \tag{6}$$

This is negative (that is, work has been performed *by* our engines), given that $\Delta_1 > \Delta_2$, *if and only if*, as can be seen from (5),

$$T_1 > T_2\left(\frac{\Delta_1}{\Delta_2}\right), \tag{7}$$

which is to be compared with the necessary condition of the classical statement of the second law that T_1 is simply greater than T_2.

One might think that the last result is just another equivalent restatement of the second law by arguing that the entropy decreased in the heat bath in stage 1 must be, according to the usual statement of the second law, less than the entropy increased in the other heat bath in stage 3,

$$\frac{\Delta Q_2}{T_2} > \frac{\Delta Q_1}{T_1}, \tag{8}$$

and by *assuming* that $\Delta Q_i = \Delta_i$, for both i, upon which (7) would have immediately followed. However, this assumption is not justifiable because the heat ΔQ_1 released by the hot heat bath, *on the average*, cannot be the same as the energy gap Δ_1 of the system at that point; and likewise for the heat absorbed by the colder reservoir. These heat amounts must be, on the average, less than the corresponding energy gaps because the heat absorbed/released by the quantum system must be moderated by the change in occupation probabilities (see Eq. (3)), but such a change in the occupation probability for a specific level is always less than one. In other words, the energy gaps Δ_i's are the maximum energy transfers possible in any exchange but the probability distributions in thermal equilibrium will not allow those maximum values to be reached. However, the result (7) is *consistent* with the second law (8) in the sense that it can be derived from (8) if ΔQ_i is proportional to Δ_i and if the proportionality constants (which are less than one) are the same for both $i = 1, 2$. But such a proportionality is extra ingredient to the second law (8), and is a consequence of the same cause that also leads to (7). Consequently, our derived result (7) is a refinement of the classical statement of the second law, and not simply a restatement in another equivalent form.

The expressions (4) and (7) not only confirm the broad validity of the second law but also refine the law further in specifying how much T_1 needs to be larger than T_2 before some work can be extracted. In other words, *work cannot be extracted, on the average, even when* T_1 *is greater than* T_2 *but less than* $T_2(\Delta_1/\Delta_2)$, in contradistinction to the classical requirement that T_1 only needs to be larger than T_2. The refinement factor (Δ_1/Δ_2) is necessarily greater than unity (by the requirement of energy conservation) and is dictated by the quantum structure of the heat engines.

This result may be extended to multi-level quantum heat engines with appropriate energy gaps, provided the quantum energy levels involved are discrete. (See also [16].) We show:

- in Section 10 the analogous condition $T_1 > T_2\,(\omega_1/\omega_2)$ for quantum simple harmonic oscillators — where ω_1 and ω_2 are, respectively, the frequencies of the oscillators in the equivalence of stages 1 and 3 above (with $\omega_1 > \omega_2$);
- in Section 11 the condition $T_1 > T_2\,(L_2/L_1)^2$ for 1D infinite square wells — where L_1 and L_2 are, respectively, the widths of the wells at temperature T_1 and T_2 (with $L_1 < L_2$).

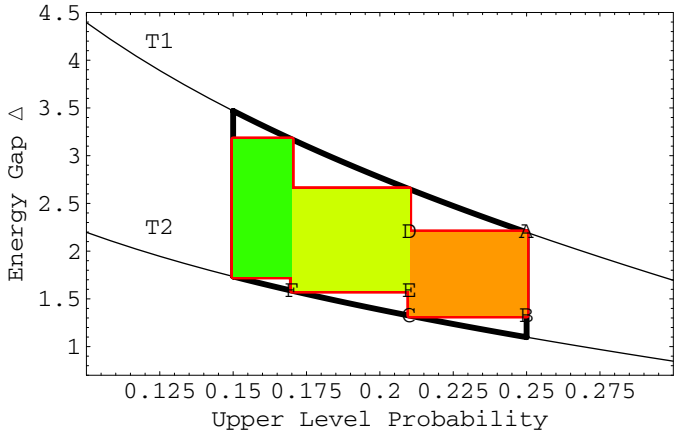

Fig. 2. Even though the quantum efficiency is always bounded by the Carnot efficiency, a quantum heat engine with asymptotically infinite number of quantum adiabatic steps can have both its efficiency and work output per cycle approaching those of the latter. This can be seen when the area of the (red) zigzag polygon approaches, from the inside, that of the irregular shape bounded by the two outermost vertical lines and the curves labeled T_1 and T_2. See text for further explanation. A colour version of the figure is available in electronic form at `http://www.eurphysj.org`.

The efficiency of the two-state engines is found to be

$$\eta_q = \frac{\Delta W_{\rm th}}{Q_{\rm in}} = \left(1 - \frac{\Delta_2}{\Delta_1}\right), \tag{9}$$

which is *independent* of temperatures and is the maximum available within the law of quantum mechanics. (A similar expression, but through a specific context, was also obtained in [25].) This expression also serves as the upper bound, with appropriate Δ_1 and Δ_2, of the efficiency of any quantum heat engine because the work performed by our heat engines through their quantum adiabatic processes is the maximum that can be extracted.

The efficiency is, as a consequence of (7), less than that of the classical Carnot engines, η_C,

$$\eta_q < 1 - T_2/T_1 \equiv \eta_C. \tag{10}$$

This is in agreement with a general fact established by Lloyd [23] that quantum efficiency must be reduced as more information is obtained about the system either by measurement or decoherence. Lloyd argues that when the system is in a fully measured or decohered state (that is, when the density matrix is already diagonalised with respect to a measured or preferred basis) then no further information can be introduced, whence the Carnot efficiency might thus be achieved.

However, the limiting Carnot efficiency may also be approached in the quantum mechanical framework through the limit of an infinite number of quantum adiabatic processes [8,11,14]. We illustrate this fact for our quantum heat engines in Figure 2. A similar discussion can also be found with the heat engines of [14].

Figure 2 depicts the inverses of (5),

$$\Delta = kT \ln\left(\frac{1}{\tilde{p}} - 1\right), \tag{11}$$

with the labels T_1 and T_2 correspond to the two temperatures. The rectangle $ABCD$ represents a particular operation of our quantum heat engines between two heat baths T_1 and T_2 — with stage 2 represented by the segment AB (which is adiabatic with no change in the probability); stage 3 by BC (no work done with constant energy gap); stage 4 by CD; and stage 1 by DA, completing an engine cycle. The area of $ABCD$, by virture of (4), represents the work derivable from this operation, which is less than the area bounded by the two vertical lines AB and CD and the two curves, which in turn is the work derivable from a corresponding Carnot engine also operated between the two temperatures.

Now, we modify our heat engines to have AB as the adiabatic expansion, BC the heat exchange, CE the adiabatic compression, EF the heat exchange, and so on. When the division becomes finer and finer with more and more steps, the area of the (red) zigzag polygon will approach, from the inside, that of the irregular shape bounded by the outermost two vertical lines and two horizontal curves. This is the limit when our modified quantum heat engine can have both the same work output per cycle and the same efficiency as those of a corresponding Carnot engine.

We think that this approach will have some interesting consequences in the context of quantum information and hope to be able to present further analysis on this limiting scenario elsewhere.

6 Transition to thermal steady states

Given that the efficiency is bounded by that of Carnot engines, which is another manifestation of the second law, can we derive more work (with a larger heat input so that the efficiency bound is maintained) than that obtainable from the thermal steady states? In the transient states approaching the thermal equilibria in stages 1 and 3 of a quantum heat engines' cycle, the density matrix elements with the upper eigenstate $|u\rangle$ and lower $|l\rangle$ satisfy the following equations [26], for $i = 1, 2$,

$$\begin{aligned}
\partial_t \rho_{uu}^{(i)} &= -(\bar{n}_i + 1)\Gamma \rho_{uu}^{(i)} + \bar{n}_i \Gamma \rho_{ll}^{(i)}, \\
\partial_t \rho_{ll}^{(i)} &= -\bar{n}_i \Gamma \rho_{ll}^{(i)} + (\bar{n}_i + 1)\Gamma \rho_{uu}^{(i)}, \\
\partial_t \rho_{ul}^{(i)} &= \partial_t \left(\rho_{lu}^{(i)}\right)^* = -\left(\bar{n}_i + \frac{1}{2}\right)\Gamma \rho_{ul}^{(i)},
\end{aligned} \tag{12}$$

under the Markovian assumption and the rotating-wave approximation and in which the heat bath is treated as a collection of infinite number of simple harmonic oscillators. In the above, Γ is the decay rate and we have assumed that the thermal average boson number in the heat bath having frequency $\nu_i = \Delta_i/h$ is

$$\bar{n}_i = \frac{1}{e^{\frac{\Delta_i}{kT_i}} - 1}. \tag{13}$$

The solution for the differential equations above with the heat bath at T_i is

$$\rho_{uu}^{(i)}(t) = e^{-(2\bar{n}_i+1)\Gamma t}\left(\rho_{uu}^{(i)}(0) - \tilde{p}_u^{(i)}\right) + \tilde{p}_u^{(i)}. \quad (14)$$

Let the system stay in contact with the heat bath at temperature T_1 in stage 1 for a time τ_1 (without achieving thermalisation); and for a time τ_2 at T_2 in stage 2. The cyclicity of the quantum heat engines requires that

$$\rho_{uu}^{(1)}(0) = \rho_{uu}^{(2)}(\tau_2), \quad \rho_{uu}^{(2)}(0) = \rho_{uu}^{(1)}(\tau_1). \quad (15)$$

This requirement together with that of $\tilde{p}_u^{(1)} > \tilde{p}_u^{(2)}$ imply, from (14),

$$0 < \rho_{uu}^{(1)}(\tau_1) - \rho_{uu}^{(2)}(\tau_2) < \tilde{p}_u^{(1)} - \tilde{p}_u^{(2)}, \quad (16)$$

for finite τ_1 and τ_2. Subsequently, the work, $|\Delta W_{\rm tr}|$, that can be derived from transient states at finite τ_1 and τ_2 is always less than that from thermal equilibrium, $|\Delta W_{\rm th}|$,

$$\begin{aligned} |\Delta W_{\rm tr}| &= \left(\rho_{uu}^{(1)}(\tau_1) - \rho_{uu}^{(2)}(\tau_2)\right)(\Delta_1 - \Delta_2)\,, \\ &< \left(\tilde{p}_u^{(1)} - \tilde{p}_u^{(2)}\right)(\Delta_1 - \Delta_2)\,, \\ &< |\Delta W_{\rm th}|\,. \end{aligned} \quad (17)$$

We suspect that, as long as the assumption of Gibbs distributions is made for the heat baths, a non-Markovian treatment or dropping the rotating wave approximation would not change this last result. Nonetheless, we present in the next section a modification of the quantum heat engines which can better the work derivation than that which is maximally available from thermal equilibrium.

7 Maximising the work extraction

Inspired and motivated by the Rabi flopping for two-level systems, see [26] for example, we present in this section a modification of the engines such that more work than usual can be derived from *thermal heat sources* (as contrast to a single-Fock-state field that drives the Rabi flopping), but at the same time more heat input would be needed in such a way that the Carnot efficiency is still a valid upper bound. That is, no violation of second law is claimed here despite of the enhanced work output.

A scenario for maximizing the work output from our quantum heat engines is as follows. Firstly, the system is prepared to be in the lower state and then subject to a radiation field in a Fock state which has exactly n_1 quanta with a frequency in resonance with the energy gap Δ_1. After some fixed time τ_1, depending on the system-field coupling strength and on the number n_1, Rabi oscillations driven by the radiation field will bring the system to the upper energy state with certainty. At this point the system can be removed from the field to perform some work in an adiabatic process which reduces the energy gap to Δ_2. Then it is next subject to another field of Fock state $|n_2\rangle$ which has a frequency in resonance with the new gap Δ_2.

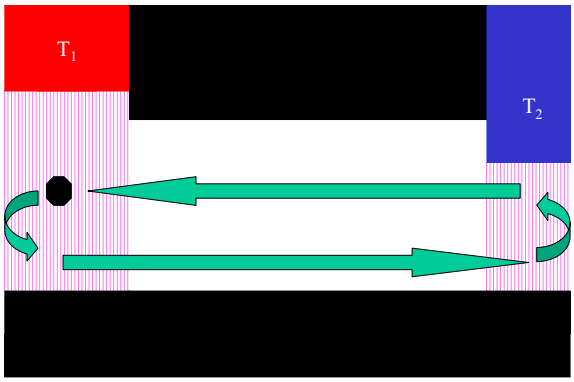

Fig. 3. A single-mode cavity is in thermal equilibrium with a bath of black-body radiation at temperature T_1. A two-state quantum system spends some time in the cavity whose mode matches the energy gap Δ_1 between its two states. After some prescribed time, it leaves the cavity and performs work in an quantum adiabatic process. It then enters another single-mode cavity which is in thermal equilibrium with another bath of black-body radiation at temperature T_2 and whose mode matches the new energy gap Δ_2. After a carefully controlled time, it leaves the cavity and moves quantum adiabatically back to the first cavity, having work done on it to have the energy gap increases back to Δ_1. With precise control of the time duration spent in each cavity, the system can extract more work in a cycle than it can if it is otherwise let to thermally equilibrate with the two heat baths in turn.

After some time τ_2 the system will be in the lower state with certainty; upon which it can be decoupled for an adiabatic compression to complete a cycle of the operation.

In effect, the steps above will remove the probability difference factor in (4), ensuring that a net work of $(\Delta_1 - \Delta_2)$ is derived in each cycle. The key point here, however, is that a Fock-state field is *not* a thermal field, and extra work or extra information would be required to maintain the Fock state such that the net book keeping (when full cyclicity is strictly enforced) will show that we cannot ultimately violate the second law.

Let us exploit this Rabi mechanism and see how it will behave in a thermal field.

A cycle of the modified quantum heat engine is depicted in Figure 3. It also consists of four stages, of which stage 2 and stage 4 remain the same as described in Section 3, whereas stages 1 and 3 are replaced respectively by:

- *stage 1':* the system has a probability $p_u^{(1)}(0)$ to be in its upper state. It is entered to a single-mode cavity which is tuned to match the energy gap Δ_1 of the system and which is in thermal equilibrium with a heat bath at temperature T_1. The average occupation of the only mode survived in the cavity has thus a (Bose-Einstein) thermal distribution $\bar{n}_1$ given by expression (13). After some carefully controlled time interval τ_1, the system is removed from the cavity to enter stage 2. The probability to find the system in it upper state is now $p_u^{(1)}(\tau_1)$. Note that, as discussed previously, only heat could be transferred in this stage

to yield a change in the occupation probabilities, and no work done as there is no change in the values of the energy levels. This stage is depicted on the left hand side of Figure 3;

- *stage 3':* the system has a probability $p_u^{(2)}(0)$ to be in its upper state. It is entered into another single-mode cavity which is in thermal equilibrium with another heat bath at temperature T_2 and which is tuned to match the new energy gap Δ_2 of the system. The average occupation of the only mode survived in the cavity has thus a (Bose-Einstein) thermal distribution $\bar{n}_2$ given by expression (13). After some carefully controlled time interval τ_2, the system is removed from the cavity to enter stage 4. The probability to find the system in it upper state is now $p_u^{(2)}(\tau_2)$. This is depicted on the right hand side of Figure 3. Some heat is thus transferred but no work is performed in this stage.

With the quantum adiabatic processes in stage 2 and stage 4, the cyclicity of the heat engines demands that

$$p_u^{(1)}(0) = p_u^{(2)}(\tau_2), \quad p_u^{(2)}(0) = p_u^{(1)}(\tau_1). \tag{18}$$

On the other hand, the exit probability can be obtained as, with $i = 1, 2$,

$$\begin{aligned} p_u^{(i)}(t) &= (\text{initial probability in } |u_i\rangle) \\ &\quad \times (\text{transition probability from } |u_i\rangle \text{ to } |u_i\rangle \text{ in } t) \\ &\quad + (\text{initial probability in } |l_i\rangle) \\ &\quad \times (\text{transition probability from } |l_i\rangle \text{ to } |u_i\rangle \text{ in } t)\,, \\ &= p_u^{(i)}(0)|\langle u_i|\psi_u^{(i)}(t)\rangle|^2 \\ &\quad + \left(1 - p_u^{(i)}(0)\right)|\langle u_i|\psi_l^{(i)}(t)\rangle|^2. \end{aligned} \tag{19}$$

$|\psi_{u(l)}^{(i)}(t)\rangle$ is the state which starts out in the upper (lower) state — i.e., $|\psi_u^{(i)}(0)\rangle = |u_i\rangle$ and $|\psi_l^{(i)}(0)\rangle = |l_i\rangle$ in the cavity at temperature T_i.

With the thermal distribution (13) assumed for the heat baths in contact with the cavities, the probability to find exactly n photons of frequency Δ_i/h in the cavity at temperature T_i is

$$P_n(T_i) = \frac{1}{1+\bar{n}_i}\left(\frac{\bar{n}_i}{1+\bar{n}_i}\right)^n. \tag{20}$$

In each of the cavities so described, the state of the engines satisfies the Schrödinger equation for a single two-level system interacting with a single-mode field which has the frequency matching the engine's energy gap,

$$i\hbar\frac{\partial|\psi^{(i)}\rangle}{\partial t} = \hbar g\left(\sigma_+^{(i)}a^{(i)} + \sigma_-^{(i)}a^{(i)\dagger}\right)|\psi^{(i)}\rangle,\ i = 1, 2, \tag{21}$$

with g is the coupling constant between the the quantum heat engine and the cavity mode, and the operators $\sigma_\pm = (\sigma_x \pm i\sigma_y)/2$ act on the two-state space of the engine and a and $a^\dagger$ are the operators on the Fock space of the field. The solution of this Schrödinger equation is given in [26], from which we derive, through (19) and (20), the probabilities

$$\begin{aligned} p_u^{(i)}(t) &= \frac{(1+2\bar{n}_i)\,p_u^{(i)}(0) - \bar{n}_i}{(1+\bar{n}_i)}\sum_{n=0}^{\infty}P_n(T_i)\cos^2(\Omega_n t) \\ &\quad + \frac{\bar{n}_i(1-p_u^{(i)}(0))}{1+\bar{n}_i}, \\ &:= A_i\sum_{n=0}^{\infty}P_n(T_i)\cos^2(\Omega_n t) + B_i, \end{aligned} \tag{22}$$

where $\Omega_n = g\sqrt{n+1}$.

Note that when the sum on the rhs of the last equation collapses to a single summand term, $P_n(T_i) \to \delta(n - n_0)$, corresponding to the radiation field being in some Fock state $|n_0\rangle$, then we will have recovered the Rabi oscillation in the level populations, which could then be exploited to apparently derive more work than otherwise allowed by the second law, but this is only apparent and cannot violate the law at all as discussed earlier.

From the last expression we can find the bounds, as functions of the initial probability $p_u^{(i)}(0)$ and the temperature T_i, of the probability $p_u^{(i)}(t)$ *for all* t. Figure 4 depicts these bounds. The probability for the system to be in the upper state upon leaving a single-mode cavity in contact with a heat bath as a function of the initial probability (upon entering the heat bath) is only accessible in the bounded areas (of red and blue).

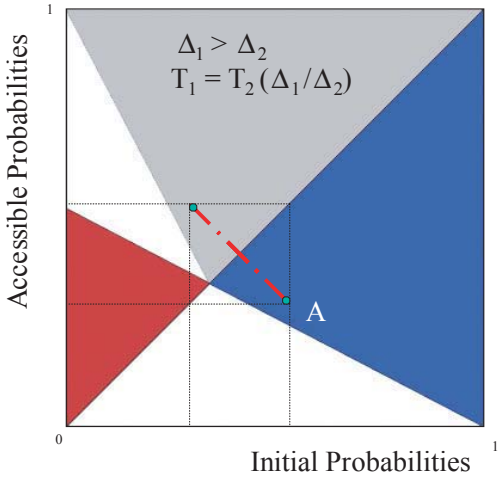

Fig. 4. For the cavity in contact with a heat sink at T_2 where we want the initial probability to be lowered upon leaving, the accessible leaving probability is bounded in the (blue) area under the diagonal, with its reflection shown in gray above the diagonal. The bounded (red) area above the diagonal is for the cavity in contact with a heat bath at $T_1 = T_2(\Delta_1/\Delta_2)$. The reflection of the point A at T_2 across the diagonal is clearly not in the accessible region at T_1, as there is no overlapping of the two regions above the diagonal. So we *cannot* form a cyclic quantum heat engine which does work at these temperatures, *even when* T_1 *is greater than* T_2 *by a factor* (Δ_1/Δ_2). A colour version of the figure is available in electronic form at `http://www.eurphysj.org`.

- For $p_u^{(i)}(0) \geq p_{\text{critical}}^{(i)}$, where

$$p_{\text{critical}}^{(i)} = \frac{\bar{n}_i}{1+2\bar{n}_i}, \tag{23}$$

the coefficient A_i of the first term in (22) is positive, and so is the first term itself. Thus, for all t,

$$B_i \leq p_u^{(i)}(t) \leq A_i \sum_{n=0}^{\infty} P_n(T_i) + B_i = A_i + B_i, \tag{24}$$

because of the normalisation $\sum_{n=0}^{\infty} P_n(T_i) = 1$. Substitution of A_i and B_i yields

$$\frac{\bar{n}_i(1-p_u^{(i)}(0))}{1+\bar{n}_i} \leq p_u^{(i)}(t) \leq p_u^{(i)}(0), \quad \text{for } p_{\text{critical}}^{(i)} \leq p_u^{(i)}(0) \leq 1. \tag{25}$$

This bounded region is depicted (in blue) in Figure 4.

- For $p_u^{(i)}(0) \leq p_{\text{critical}}^{(i)}$, the coefficient A_i is negative, and so is the first term. Thus, for all t,

$$A_i + B_i \leq p_u^{(i)}(t) \leq B_i. \tag{26}$$

That is,

$$p_u^{(i)}(0) \leq p_u^{(i)}(t) \leq \frac{\bar{n}_i(1-p_u^{(i)}(0))}{1+\bar{n}_i}, \quad \text{for } 0 \leq p_u^{(i)}(0) \leq p_{\text{critical}}^{(i)}. \tag{27}$$

This bounded region is also depicted (in red) in the same figure.

Note also that the vertex on the diagonal separating these two regions determines the stationary point where the probability is time independent and is equal to the initial probability. As the thermal equilibrium probability given by the Gibbs distribution must be independent of both time and initial probability, it is represented by a horizontal line crossing this vertex.

For the cavity in contact with the heat bath at T_1, we want to have the exit probability to be greater (the greater, the more work can be extracted) than the initial probability,

$$p_u^{(1)}(\tau_1) > p_u^{(1)}(0) = p_u^{(2)}(\tau_2), \tag{28}$$

thus we need only to consider the appropriate portion of the bounds for this cavity, namely that above the diagonal. Reversely, for the cavity in contact with the heat bath at T_2, we want to have the exit probability to be smaller (the smaller, the better) than the initial probability,

$$p_u^{(2)}(\tau_2) < p_u^{(2)}(0) = p_u^{(1)}(\tau_1), \tag{29}$$

hence for this cavity we need only to consider the other portion of the bounds below the diagonal. Thus, we can also use this Figure 4 to elucidate the situation for the two heat baths in which $T_1 = T_2(\Delta_1/\Delta_2)$, the (red) area above the diagonal comes from T_1 and the (blue) below the diagonal from T_2. The coordinate of a point A in the (blue) area below the diagonal in Figure 4 is $(p_u^{(2)}(0), p_u^{(2)}(\tau_2))$, representing an exit probability less than the entry one at the cavity with temperature T_2. The corresponding point at temperature T_1 must have, by requirement of cyclicity, the coordinate

$$\left(p_u^{(1)}(0), p_u^{(1)}(\tau_1)\right) = \left(p_u^{(2)}(\tau_2), p_u^{(2)}(0)\right), \tag{30}$$

which thus is the reflection of the point A across the diagonal. The gray area above the diagonal in Figure 4 is the reflection of the (blue) area for T_2. However, it is clearly seen that for $T_1 = T_2(\Delta_1/\Delta_2)$ this reflection is *not* in the accessible (red) area for T_1. We then conclude that at these temperatures, *even with* T_1 *greater than* T_2 *by a factor* (Δ_1/Δ_2), the quantum heat engines *cannot* do work *on the average*. As a consequence of the temperature-independent efficiency similar to (9), the engines can neither absorb nor transfer any heat.

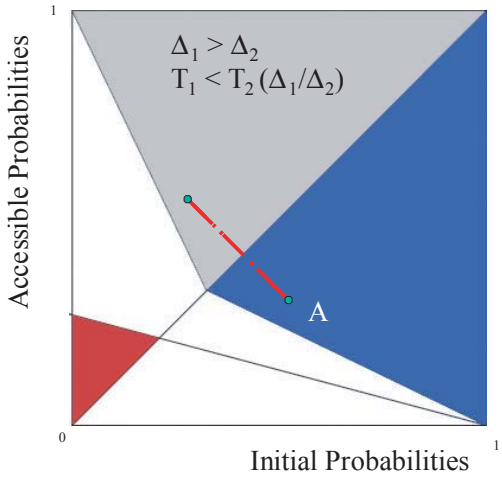

Fig. 5. Similar to Figure 4 but this time with $T_1 < T_2(\Delta_1/\Delta_2)$. Once again we cannot have a cyclic quantum heat engine, even for T_1 in the range $T_2 < T_1 < T_2(\Delta_1/\Delta_2)$. A colour version of the figure is available in electronic form at `http://www.eurphysj.org`.

In Figure 5, we combine the relevant bounds for T_2 below the diagonal (in blue) and those for T_1 above the diagonal (in red) for the choice $T_1 < T_2(\Delta_1/\Delta_2)$. It is seen once again that no work is derivable on the average. Not only we have thus confirmed the second law that, *on the average*, no process is possible whose *sole* result is the transfer of heat from a cooler to a hotter body, with or without a production of work. But we have also clarified the degrees of coolness and hotness in terms of the quantum energy gaps involved before such a process is possible; namely, we must have $T_1 > T_2(\Delta_1/\Delta_2)$, as in (7) once again.

We now show how our quantum heat engines are capable of performing more work than can be derived from thermal equilibrium otherwise. In Figure 6, which combines the case $T_1 > T_2(\Delta_1/\Delta_2)$, there is some overlap between the (red) area for T_1 and the reflection of the area

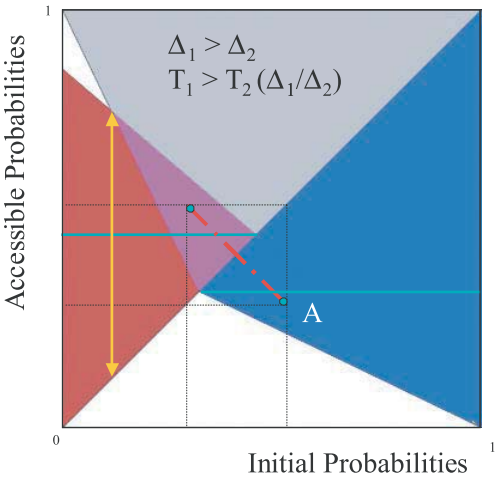

Fig. 6. Similar to Figure 4 but this time with $T_1 > T_2(\Delta_1/\Delta_2) > T_2$. We can form a cyclic quantum heat engine at these temperatures, in broad agreement with the classical statement of second law. The maximum work that can be extracted in a single cycle is proportional to the length of the (yellow) vertical double arrow and is more than that for thermally equilibrated situation, which is proportional to the distance between the two horizontal (green) lines which represent the thermal equilibrium probabilities for these T_1 and T_2 respectively. A colour version of the figure is available in electronic form at `http://www.eurphysj.org`.

for T_2 across the diagonal. In this case, it can be seen that the production of some work, $\Delta W_{\rm cav}$, is now possible,

$$|\Delta W_{\rm cav}| = \left(p_u^{(1)}(\tau_1) - p_u^{(2)}(\tau_2)\right)(\Delta_1 - \Delta_2)\,. \quad (31)$$

In general, if and when we choose to operate with a point below the thermal equilibrium line in the (blue) area for T_2 such that its reflection across the diagonal is above the thermal equilibrium line in the (red) area for T_1 as shown in the figure, we can derive more work than the case of thermal equilibrium. The work done is proportional to the difference in probabilities as shown in (4) and (31). Here $|\Delta W_{\rm cav}|$ is greater than the work derivable at thermal equilibrium, $|\Delta W_{\rm th}|$, because the vertical distance between point A and its reflection in Figure 6 is greater than the vertical distance between the two horizontal lines, which represent the two thermal equilibria.

From the bounds (25) and (27), we can evaluate the maximum amount of work extractable from our modified quantum heat engines at given temperatures

$$\frac{\max|\Delta W_{\rm cav}|}{|\Delta W_{\rm th}|} = \frac{(1+2\bar{n}_1)(1+2\bar{n}_2)}{(1+\bar{n}_1+\bar{n}_2)} > 1. \quad (32)$$

This is the upper limit we could obtain when the switching on and off of the system-field coupling can be done in such an adiabatic manner that the total associated work for switching can be made arbitrarily small. Nonadiabatic or sudden switching requires some work input specific for the situation, which would lessen the ratio above.

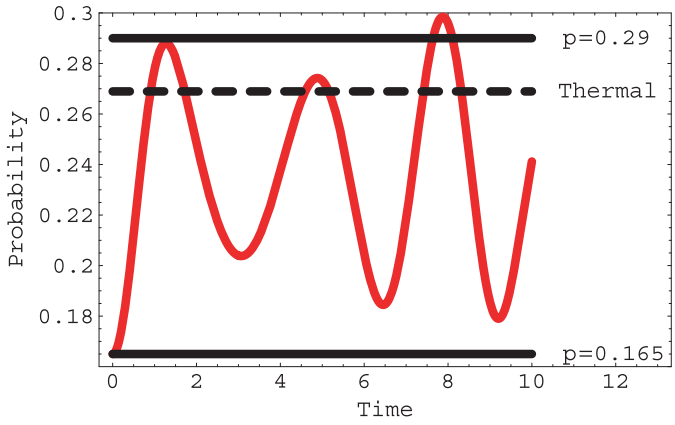

Fig. 7. $p_u^{(1)}$ versus time according to equation (22). The system enters a single-mode cavity, in contact with a heat source at temperature T_1 (here, $kT_1/\Delta_1 = 1.5$), with the probability in the upper state $p_u^{(1)}(0) = 0.165$ $(= p_u^{(2)}(\tau_2)$, by cyclicity requirement) and leaves the cavity, at suitably chosen time τ_1, with the increased probability $p_u^{(1)}(\tau_1) = 0.29$. This latter probability is larger than the thermal equilibrium probability at this temperature (dashed line).

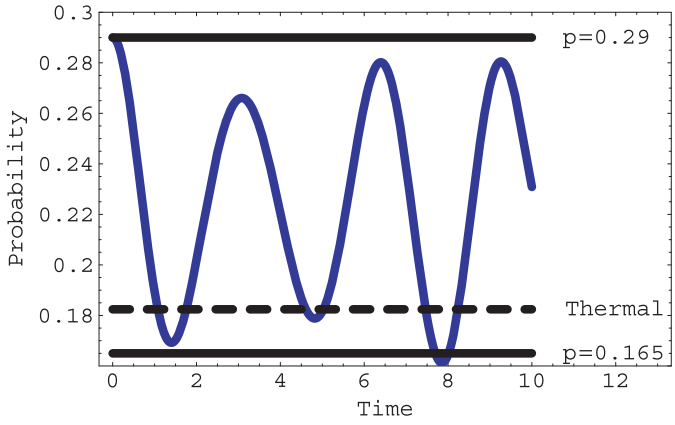

Fig. 8. $p_u^{(2)}$ versus time. Similar to Figure 7 but this time the probability upon entering a cavity, in contact with a heat sink at temperature $T_2 < T_1(\Delta_2/\Delta_1) < T_1$ (here, $kT_2/\Delta_2 = 1.0$), is $p_u^{(2)}(0) = 0.29$ $(= p_u^{(1)}(\tau_1)$, by cyclicity requirement) and upon leaving, at suitably chosen time τ_2, is $p_u^{(2)}(\tau_2) = 0.165$, completing a cycle of the quantum heat engine. The latter probability is lower than the thermal equilibrium probability at this temperature (dashed line), thus allowing more work to be extracted.

8 An illustration

As an illustration that we can choose and a priori fix the time τ_1 and τ_2 for all the cycles of the modified mode of operation for our quantum heat engines such that more work can be derived than otherwise available from thermal equilibrium, we present herein the example in Figures 7 and 8. These numerical results are obtained from (22) with $g = 1$ and other parameters as stated in the captions. Note that in Figure 7 the probability at subsequent time is always more than that of the initial time, in agreement with the fact that the (red) area for T_1 is above the diagonal

in Figure 6. The reverse is true for Figure 8, because the (blue) area for T_2 is below the diagonal in Figure 6.

9 Maxwell's daemon revisited

The expression (22) for the probability, derived from (19), requires some careful justifications. Following [26], we expand the state vector $|\psi\rangle$ (dropping the superscript (i)) in terms of $|u,n\rangle$, in which the engine is in the upper state $|u\rangle$ and the field has exactly n photons, and of $|l,n\rangle$ in which the engine is in the lower state $|l\rangle$,

$$|\psi\rangle = \sum_n \left(c_{u,n}(t)|u,n\rangle + c_{l,n}(t)|l,n\rangle\right). \tag{33}$$

From this, the Schrödinger equation (21) can now be replaced by

$$\dot{c}_{u,n} = -ig\sqrt{n+1}\, c_{l,n+1}, \quad \dot{c}_{l,n+1} = -ig\sqrt{n+1}\, c_{u,n}. \tag{34}$$

The general solutions for these probability amplitudes are

$$\begin{aligned} c_{u,n}(t) &= c_{u,n}(0)\cos(\Omega_n t) - ic_{l,n+1}(0)\sin(\Omega_n t), \\ c_{l,n+1}(t) &= c_{l,n+1}(0)\cos(\Omega_n t) - ic_{u,n}(0)\sin(\Omega_n t), \end{aligned} \tag{35}$$

in which the initial probability amplitudes are assumed to be factorised,

$$\begin{aligned} c_{u,n}(0) &= \sqrt{p_u(0)}\sqrt{P_n}, \\ c_{l,n+1}(0) &= e^{i\theta_s}\sqrt{1-p_u(0)}e^{i\theta_f}\sqrt{P_{n+1}}, \end{aligned} \tag{36}$$

where the relative phases θ_s for the engine and θ_f for the field, respectively, are not zero in general.

Now, we can also express the probability on the lhs of (22) as

$$p_u(t) = \sum_n |c_{u,n}(t)|^2. \tag{37}$$

Direct substitution of the amplitudes above, however, leads an additional cross term which does not exist on the rhs of expression (22) but is proportional to

$$\sim \Re\Bigg(ie^{i\theta_s}\sqrt{p_u(0)\left(1-p_u(0)\right)} \times \sum_n e^{i\theta_f}\sqrt{P_n P_{n+1}}\cos(\Omega_n t)\sin(\Omega_n t)\Bigg). \tag{38}$$

Accordingly, the various bounds for $p_u(t)$ will be modified by the term $\sqrt{p_u(0)\left(1-p_u(0)\right)}$, which is nonlinear in $p_u(0)$, unlike the situation in (25, 27) depicted in Figure 4, from which the second law was seen to be followed. One might think that this extra non-linear term could be exploited to beat the second law (thanks to the newly emerged overlapping of regions which were not overlapped previously in Fig. 4). But this is not meant to be, however. The reason for this impossibility is that, in general, the various phases in (38) are not fixed but can be random, especially for the phase θ_f of the thermal field. They will have to be averaged over, rendering the cross term (38) vanished after all. We thus get back the expression (22) exactly.

If the phases could be controlled physically then the second law might be violated. But the point to be emphasised here is that such a control of the phases will require some careful operation which is nothing more than just another disguised act of Maxwell's daemon. In the end, any such resulted violation of the second law, if possible, is not and should not be surprising at all.

10 Quantum heat engines with 1-D simple harmonic oscillators

We now generalise some of the above results to quantum systems having an infinite number of energy levels. Firstly, we consider a 1-D simple harmonic oscillator of frequency ω_1 in thermal equilibrium with a heat bath at T_1. The oscillator is then removed from the heat bath to undergo a quantum adiabatic expansion until its frequency is dropped to ω_2. It is then equilibrated with another heat bath at temperature T_2 before undergone another quantum adiabatic compression to raise its frequency back to ω_1. In one such cycle, the oscillator performs an amount of work,

$$\begin{aligned} \Delta W &= \sum_{n=0}^{\infty}\left(E_n^{(1)} - E_n^{(2)}\right)\left(p_n^{(2)} - p_n^{(1)}\right), \\ &= \hbar\left(\omega_1 - \omega_2\right)\sum_{n=0}^{\infty}\left(n+\frac{1}{2}\right)\left(p_n^{(2)} - p_n^{(1)}\right), \\ &= \hbar\left(\omega_1 - \omega_2\right)\sum_{n=0}^{\infty} n\left(p_n^{(2)} - p_n^{(1)}\right), \end{aligned} \tag{39}$$

with the Gibbs distributions for $i = 1, 2$

$$p_n^{(i)} = \left(1 - e^{-\alpha_i}\right)e^{-n\alpha_i}, \tag{40}$$

and

$$\alpha_i = \frac{\hbar\omega_i}{kT_i}. \tag{41}$$

We have used the energy expressions for simple harmonic oscillators

$$E_n^{(i)} = \left(n+\frac{1}{2}\right)\hbar\omega_i. \tag{42}$$

Let

$$x = \alpha_2 - \alpha_1 \tag{43}$$

and consider the sum in (39) as a function of x,

$$f(x) = \sum_{n=0}^{\infty} n\left\{\left(1 - e^{-\alpha_1 - x}\right)e^{-n\alpha_1 - nx} - \left(1 - e^{-\alpha_1}\right)e^{-n\alpha_1}\right\}. \tag{44}$$

Its derivative is

$$f'(x) = -\sum_{m=1}^{\infty} m e^{-m(\alpha_1+x)}, \tag{45}$$

which is always negative (we always have $x > -\alpha_1$ for the convergence of the infinite sum, as $\alpha_2 > 0$). Thus $f(x)$ is a monotonically decreasing function; in particular, $f(x) < f(0) = 0$ for $x \geq 0$. From the definition of x (43) and $f(x)$ (44) we conclude that the oscillator can only perform work on the environment (i.e. when $f(x) < 0$) *if and only if* $x > 0$, which means that $\alpha_2 > \alpha_1$. That is,

$$T_1 > T_2 \left(\frac{\omega_1}{\omega_2}\right) \tag{46}$$

is the necessary and sufficient condition for work to be performed by a quantum simple harmonic oscillator in such a cycle described above.

11 Quantum heat engines with 1-D infinite square wells

Similarly to the last section, but we now replace the oscillator by a particle of mass m in an 1-D infinite square well. The work performed in a cycle is also

$$\Delta W = \sum_{n=0}^{\infty} \left(E_n^{(1)} - E_n^{(2)}\right)\left(p_n^{(2)} - p_n^{(1)}\right), \tag{47}$$

but this time with the energies

$$E_n^{(i)} = n^2 \frac{\hbar^2\pi^2}{2mL_i^2} \tag{48}$$

and the thermal distributions

$$p_n^{(i)} = \frac{e^{-n^2\gamma_i}}{\sum_m e^{-m^2\gamma_i}} \equiv \frac{e^{-n^2\gamma_i}}{Z_i}, \tag{49}$$

where $\gamma_i = \hbar^2\pi^2/(2mkT_iL_i^2)$ and L_i are the widths of the wells at T_i. Thus, expression (47) becomes

$$\Delta W = \frac{\hbar^2\pi^2}{2m}\left(\frac{1}{L_1^2} - \frac{1}{L_2^2}\right)\sum_{n=0}^{\infty} n^2\left(p_n^{(2)} - p_n^{(1)}\right). \tag{50}$$

Let

$$y = \gamma_2 - \gamma_1, \tag{51}$$

and consider the infinite sum on the rhs of (50) as a function g of y. Its derivative wrt y is

$$\begin{aligned} g'(y) &= -\sum_n n^4 \frac{e^{-n^2(\gamma_1+y)}}{Z_2} + \left\{\sum_n n^2 \frac{e^{-n^2(\gamma_1+y)}}{Z_2}\right\}^2, \\ &= -\langle (n^2)^2\rangle_y + \left(\langle n^2\rangle_y\right)^2, \end{aligned} \tag{52}$$

where

$$\langle O\rangle_y \equiv \sum_n O_n \frac{e^{-n^2(\gamma_1+y)}}{Z_2}. \tag{53}$$

It follows directly from (52) that $g'(y) < 0$. Noting that $g(0) = 0$, we thus have $g(y) < g(0) = 0$, that is, $\Delta W < 0$, *if and only if* $y > 0$. In other words, the condition upon which the system *can* do work is *if and only if*

$$T_1 > T_2 \left(\frac{L_2}{L_1}\right)^2. \tag{54}$$

Once again, this is clearly a refinement of the second law of thermodynamics for this kind of quantum heat engines.

It is straightforward to generalise the consideration above to some particular cases of continuous spectra. Let the energy spectrum of a quantum system to be used for the quantum heat engine be continuous and be able to be indexed by a continuous variable α in such a way that

$$E(\alpha) = h(\alpha)k(\text{generalised extensive coordinates } \vec{x}). \tag{55}$$

$h(\alpha)$ is the generalised form of the discrete n of the simple harmonic oscillators or n^2 of the infinite wells considered above. The work done in a cycle analogous to (47) is

$$\Delta W = (k(\vec{x}_1) - k(\vec{x}_2)) \int d\alpha h(\alpha)\left(\frac{e^{-h(\alpha)k(\vec{x}_2)/(kT_2)}}{Z_2} - \frac{e^{-h(\alpha)k(\vec{x}_1)/(kT_1)}}{Z_1}\right), \tag{56}$$

where Z_i are the partition functions

$$Z_i = \int d\alpha\, e^{-h(\alpha)k(\vec{x}_i)/(kT_i)}. \tag{57}$$

Now it is a simple matter to repeat the last few steps leading to (54) above to show that work can be done *by* the continuous-spectrum system if and only if:

$$T_1 > T_2 \left(\frac{k(\vec{x}_1)}{k(\vec{x}_2)}\right), \tag{58}$$

where the last factor on the rhs is always greater than one, thus clarifying the second law of thermodynamics.

12 Concluding remarks

By interpreting work and heat, but without referring to entropy directly, in the quantum domain and by applying this interpretation to the simplest quantum systems, we have not only confirmed the broad validity of the second law but also been able to clarify and refine its various aspects. On the one hand, explicitly because of the probabilistic nature of quantum mechanics, there do exist physical processes which can violate certain classical statements of the second law. However, such violation only

occurs randomly in the short term and thus it cannot be exploitable nor harnessible. On the other hand, the second law is seen to be valid *on the average*. This confirmation of the second law is in accordance with the fact that, while we can treat the quantum heat engines purely and entirely as quantum mechanical systems, we still have to assume the Gibbs distributions for the heat baths involved. Such distributions can only be derived [27] with non-quantum-mechanical assumptions, which ignore, for example, any quantum entanglement within the heat baths. Indeed, it has been shown that [28,29] the law of entropy increase is a mathematical consequence of the initial states being in such general equilibrium distributions. This illustrates and highlights the connection between the second law to the unsolved problems of emergence of classicality, of quantum measurement and of decoherence which are inter-related and central to quantum mechanics. Only until some further progress is made on these problems, the classicality of the heat baths will have to be assumed and remained hidden in the assumption of the Maxwell-Boltzmann-Gibbs thermal equilibrium distributions.

Even our results support the second law, on the average, we have further clarified the degree of temperature difference (7), in terms of the quantum energy gaps involved, between the heat baths before any work can be extracted. While the Carnot efficiency is an upper bound for that of the quantum heat engines, the former could be approached by the quantum engines with the introduction of an infinite number of alternating adiabatic and heat transferred steps. The implication of this approach in the context of quantum information deserves further investigations elsewhere.

Inspired and motivated by the Rabi oscillations, we have also shown how to extract more work from the heat baths than otherwise possible with thermal equilibrium distributions — but more heat input would also be needed in such a way that the Carnot efficiency is still a valid upper bound. Note that such an operation is subject to the bounds given in (25) and (27), which then, as can be seen through their depiction in the figures, ensure that we stay within the second law, but refined with the necessary condition (7). The perfect agreement between the specific results derived from the quantum dynamical bounds (25) and (27) with the general result (7) derived from statistical mechanics is quite remarkable. We speculate that such agreement is not accidental but is once again a consequence of the Gibbs distributions assumed for the heat baths in both derivations; and the agreement should thus be independent of specific details of the quantum dynamics involved. Note also that the modified operation with single-mode cavities is not an operation of Maxwell's daemon because the information about the time intervals τ_1 and τ_2 is not conditional but is fixed and forms an integrated part of the modified engines. This information, being common to *all* cycles, need not and should not be erased after each cycle to preserve the cyclicity condition. Other studies of very different classes of quantum heat engines [13,15] have apparently claimed similar results that more work can be derived than from classical engines. (However, if the cyclicity condition is not strictly observed for a heat engine, as in the case for some of those studies, then some extra effects may be hidden or unaccounted for, such as those associated with a maintenance of some coherent states or some Fock state, and *apparent* violation of the second law might thus be possible.)

Our class of quantum heat engines can also readily offer a feasible way to physically realise Maxwell's daemon, in a way different to Szilard's engine but also through the acts of quantum measurement and information erasure. Finally, some of our results above have also been generalised to quantum heat engines having an infinite number of energy levels, or even special cases of continuous spectra. Some analysis of three-level quantum heat engines has also been available recently [16], but because of the many different energy gaps available, different conditions with different combinations of gap ratios could enter as a counterpart of (4) above.

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