

# Maximal work extraction from quantum systems

A.E. Allahverdyan<sup>1,2)</sup>, R. Balian<sup>3)</sup> and Th.M. Nieuwenhuizen<sup>1)</sup>

<sup>1)</sup> *Institute for Theoretical Physics, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

<sup>2)</sup> *Yerevan Physics Institute, Alikhanian Brothers St. 2, Yerevan 375036, Armenia and*

<sup>3)</sup> *SPhT, CEA-Saclay, 91191 Gif-sur-Yvette cedex, France*

Thermodynamics teaches that if a system initially off-equilibrium is coupled to work sources, the maximum work that it may yield is governed by its energy and entropy. For finite systems this bound is usually not reachable. The maximum extractable work compatible with quantum mechanics (“ergotropy”) is derived and expressed in terms of the density matrix and the Hamiltonian. It is related to the property of majorization: more major states can provide more work. Scenarios of work extraction that contrast the thermodynamic intuition are discussed, e.g. a state with larger entropy than another may produce more work, while correlations may increase or reduce the ergotropy.

The generality of the laws of thermodynamics for macroscopic bodies led to a long-lasting effort to derive them from microphysics<sup>1,3,4</sup>. This program is by now completed. In contrast, for finite systems, the application and even the formulation of the laws of thermodynamics are still the subject of studies<sup>5,6</sup>. The origin of qualitative differences between large and finite systems was recognized long ago<sup>7,8</sup>. A quantum system submitted to time-dependent external potentials that describe work sources undergoes a unitary transformation. During such an evolution, the density matrix has constant eigenvalues, thus it cannot become gibbsian when starting from an arbitrary initial state. In contrast, most macroscopic systems have a thermodynamic behavior: they evolve close to a Gibbs state under the effect of slowly varying external potentials, keeping nearly constant entropy<sup>8,9</sup>. This holds in general, although their evolution is Hamiltonian at the microscopic level, owing to the large and smooth density of states of the spectrum<sup>8</sup>. Accordingly, the responses of finite and of infinite systems to external perturbations differ qualitatively<sup>7</sup>. As an example, processes were studied which would be reversible in thermodynamics, but entail a specific irreversibility due to the finite size of the involved system<sup>10,11</sup>.

The problem we treat here is well known in thermodynamics. It initiated its birth in 1824: What is the maximal amount of work that can be extracted from a system  $S$  by means of an external source of work acting cyclically in a thermally isolated process? And what are the criteria for comparing different states with respect to their work-providing ability? We find answers to both questions, and show that for finite systems they qualitatively disagree with the standard thermodynamical ones.

A specific case in which a finite system  $S$  behaves thermodynamically in regard to its work production is well known. If  $S$  is initially prepared in a gibbsian state, it cannot produce work when coupled to a source of work through an external variable which returns to its initial value<sup>4,9,12</sup>. Such a state is thus called *passive*. We shall therefore be interested in off-equilibrium initial states. A scenario for preparing such states is to take  $S$  consisting of two non-interacting (or weakly interacting) subsystems, to set separately the two parts in thermal contact with

heat baths at different temperatures, and then to decouple them from the baths. Subsequent coupling with a source of work may yield an amount of work that we wish to evaluate.

The *maximal work-extraction problem* is thus posed in the following way<sup>1,2</sup>. Consider a system  $S$  which can exchange work with external macroscopic sources. The evolution of its density operator  $\rho(t)$  is then generated by a Hamiltonian  $H(t) = H + V(t)$ , where the time-dependence of  $V(t)$  accounts for work transfer. Following Refs.<sup>1,2</sup>, we call “*cyclic*” a process in which  $S$ , originally isolated, is coupled at the time  $t = 0$  to external sources of work, and decouples from them at the time  $\tau$ . Thus, the driving variables of the sources are cyclic, and the potential  $V(t)$  vanishes before  $t = 0$  and after  $\tau$ :  $V(0) = V(\tau) = 0$ . However,  $S$  need not return to its initial state at the time  $\tau$ . The system  $S$  is thermally isolated but may involve energy exchanges between its parts. The initial state  $\rho(0) = \rho_0$  and the Hamiltonian  $H$  being given, we look for the maximum work  $\mathcal{W}$  that may be extracted from  $S$  for arbitrary  $V(t)$ . According to the dynamics

$$i\hbar \dot{\rho} = [H(t), \rho(t)], \quad (1)$$

the work  $dW = \text{tr}[\rho(t) \dot{V}(t)] dt$  done on  $S$  is<sup>1,2,3</sup>

$$W = \text{tr}[\rho(\tau) H] - E(\rho_0), \quad E(\rho_0) \equiv \text{tr}[\rho_0 H] \equiv E_i. \quad (2)$$

Among all final states  $\rho(\tau)$  reached from  $\rho_0$  under the action of any potential  $V(t)$ , we are therefore looking for the one with lowest final energy  $E_f = \text{tr}[\rho(\tau) H]$ .

The standard answer<sup>1,2</sup> relies on the idea that the final state  $\rho(\tau)$  is Gibbsian and that its von Neumann entropy  $S = -\text{tr} \rho \ln \rho$  cannot decrease between the times 0 and  $\tau$ . The maximum value of the work (2) is reached when the final state has the equilibrium form

$$\rho(\tau) = \rho_{\text{eq}} = \frac{e^{-\beta H}}{Z}, \quad Z = \text{tr} e^{-\beta H}, \quad (3)$$

with  $\beta > 0$  determined by the equality of the initial and final entropies:  $\ln Z - \beta \partial \ln Z / \partial \beta = -\text{tr} \rho_0 \ln \rho_0$ . The largest amount of work  $-W$  extractable from  $S$  is thus

$$\mathcal{W}_{\text{th}} = E(\rho_0) - TS(\rho_0) + T \ln Z, \quad (4)$$

the familiar difference of free energy between initial and final state, both evaluated with the final temperature  $T$ .

*Finite systems.* The above derivation involves two arguments which call for some discussion. Following thermodynamical intuition, we have first stated that the entropy cannot decrease. In fact, the von Neumann entropy  $S(\rho)$  remains constant during the evolution (1). If  $S$  is macroscopic, it is the coarse-grained entropy which can increase. Anyhow, this point is harmless since the bound (4) corresponds to constant-entropy processes of the total system. We also implicitly assumed that  $S$  may be brought into an equilibrium state  $\rho_{\text{eq}}$  by means of some evolution (1). For macroscopic systems this is usually allowed since dissipative processes within  $S$  may occur while it evolves under the influence of the coupling  $V(t)$ .

For finite systems, the sole action of  $V(t)$  is in general not sufficient to allow reaching at the time  $\tau$  a gibbsian state of the form (3). Indeed, not only is the entropy  $S(\rho)$  conserved during the evolution generated by (1), but all the eigenvalues of  $\rho^{7,8}$ . In contrast to thermodynamic systems, finite systems keep memory of their initial state and do not involve any relaxation mechanism. One may therefore expect that the maximal amount of work  $\mathcal{W}$  extracted from  $S$  is generally smaller than  $\mathcal{W}_{\text{th}}$ .

More precisely, the evolution (1) of  $\rho$  is unitary, so that  $\rho(\tau) = U \rho_0 U^\dagger$ . We look for the minimum of the final energy  $E_f = \text{tr} U \rho_0 U^\dagger H$  over all unitary operators  $U$ . We can parameterize the variations  $\delta U$  of  $U$  as  $\delta U = XU$ , where  $X$  is an arbitrary infinitesimal antihermitian operator. Hence, we find  $\delta E_f = \text{tr}(XU \rho_0 U^\dagger H - U \rho_0 U^\dagger XH) = \text{tr} X[\rho(\tau), H]$ . The stationarity of  $E_f$  thus implies that  $\rho(\tau)$  should commute with  $H$  and have the same eigenvalues as  $\rho_0$ , a condition which replaces (3). In the spectral resolutions of  $\rho_0$  and  $H$ ,

$$\rho_0 = \sum_{j \geq 1} r_j |r_j\rangle \langle r_j|, \quad H = \sum_{k \geq 1} \varepsilon_k |\varepsilon_k\rangle \langle \varepsilon_k|, \quad (5)$$

we order the eigenvalues as

$$r_1 \geq r_2 \geq \dots, \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots \quad (6)$$

The minimum of  $E_f$  is then  $\sum_j r_j \varepsilon_j$ , and it is reached for

$$\rho(\tau) = \sum_j r_j |\varepsilon_j\rangle \langle \varepsilon_j|, \quad (7)$$

which is stationary since it commutes with  $H$ . This result is consistent with the extension for finite systems of the second law in Thomson's formulation<sup>4,9,12</sup>: the two conditions which characterize the state  $\rho(\tau)$  (commutation with  $H$  and ordering (6)) are the ones which ensure that this state is passive: no further work can be extracted from  $S$  after time  $\tau$  by means of cyclic processes.

Note that, if the spectrum of  $H$  involves degeneracies which have no counterpart in  $\rho_0$ , the final state  $\rho(\tau)$  is not unique (in contrast to  $\rho_{\text{eq}}$  associated with  $\mathcal{W}_{\text{th}}$ ).

Altogether, the maximum of the amount of work (2) that can be extracted from  $S$  is

$$\mathcal{W} = \sum_{j,k} r_j \varepsilon_k (|\langle r_j | \varepsilon_k \rangle|^2 - \delta_{jk}). \quad (8)$$

For  $\mathcal{W}$ , which depends only on the initial state and Hamiltonian, we coin the name *ergotropy* ( $\epsilon\rho\gamma ov$ : work;  $\tau\rho\sigma\pi\eta$ : transformation, turn). By construction, we have  $\mathcal{W}_{\text{th}} \geq \mathcal{W} \geq 0$ . The ergotropy  $\mathcal{W}$  vanishes if  $\rho_0$  is passive. It equals the thermodynamical upper bound  $\mathcal{W}_{\text{th}}$  only if there exist two numbers  $\beta$  and  $Z$  such that the eigenvalues (5, 6) of  $\rho_0$  and  $H$  satisfy  $\ln r_j = -\beta \varepsilon_j - \ln Z$ , so as to allow  $\rho(\tau) = U \rho_0 U^\dagger$  to reach a gibbsian form (3) in spite of the lack of thermalization mechanism. Noticeable examples include: (i) a pure initial state of  $S$ ; (ii) two-level systems; (iii) harmonic oscillators in case  $\rho_0$  is a gaussian state, since both the sequences  $\varepsilon_k$  and  $\ln r_j$  are then equidistant.

For macroscopic systems the difference  $\mathcal{W}_{\text{th}} - \mathcal{W}$  is typically relatively small, since the final state (7) may lie close to an equilibrium state if  $\tau$  is large; the spectra of  $\ln \rho_0$  and  $H$  are dense, and a linear relation between them is approximately satisfied in the relevant region. However, for finite systems  $\mathcal{W}_{\text{th}} - \mathcal{W}$  can be significant.

It remains to show that the bound  $\mathcal{W}$  can actually be reached by coupling  $S$  with some source of work that realizes a cyclic process. We thus want to find a time  $\tau$  and an interaction  $V(t)$  which vanishes at  $t = 0$  and at  $t = \tau$ , so that, when added to the Hamiltonian  $H$ ,  $V(t)$  leads from the initial state  $\rho_0$  to  $\rho(\tau)$  defined in (7). An evolution operator which realizes this goal is

$$U = \sum_j |\varepsilon_j\rangle \langle r_j|. \quad (9)$$

A Hamiltonian  $H + V(t)$  generates in the interaction representation an evolution operator  $U_I$  which satisfies

$$i\hbar \frac{dU_I(t)}{dt} = e^{iHt/\hbar} V(t) e^{-iHt/\hbar} U_I(t), \quad (10)$$

with  $U_I(0) = 1$ . We define  $U_I(\tau) \equiv e^{iH\tau/\hbar} U = e^{-i\Lambda\tau/\hbar}$ , where  $\Lambda$  is obtained by diagonalization. We choose for  $U_I(t)$  the simple form  $U_I(t) = e^{-i\Lambda\varphi(t)/\hbar}$ , where  $\varphi(0) = \dot{\varphi}(0) = \dot{\varphi}(\tau) = 0$  and  $\varphi(\tau) = \tau$ . Then the potential  $V(t) = \dot{\varphi}(t) e^{-iHt/\hbar} \Lambda e^{iHt/\hbar}$  describes according to (10) a source of work that extracts during the time  $\tau$  the work (8) from  $S$ . This potential is far from unique.

In case not only  $\rho(\tau)$  but also the initial state is stationary,  $[\rho_0, H] = 0$ , we can choose the same eigenbases for  $\rho_0$  and  $H$ , but (6) implies that  $|r_1\rangle, |r_2\rangle, \dots$  in (5) are deduced from  $|\varepsilon_1\rangle, |\varepsilon_2\rangle, \dots$  by some permutation. Then the matrix  $|\langle r_j | \varepsilon_k \rangle|^2$  in (8) is a permutation matrix. For instance, if the lowest two levels  $\varepsilon_1 < \varepsilon_2$  have initially the inverted populations  $r_2 < r_1$ , respectively, so that  $|r_1\rangle = |\varepsilon_2\rangle$  and  $|r_2\rangle = |\varepsilon_1\rangle$ , we may easily implement the transformation  $U$ , a permutation that interchanges  $r_1$  and  $r_2$ , either in a rapid or in a quasistatic regime.

*Comparison of activities.* We wish to compare two states  $\rho_0$  and  $\sigma_0$  of a system  $S$  as regards the maximum work that they may provide. To make such a comparison meaningful, we assume the initial energies to be the same,  $E(\rho_0) = E(\sigma_0)$ . If  $S$  is macroscopic and can reach equilibrium at the end of the process,  $\mathcal{W}_{\text{th}}$

depends only on the entropy  $S$  of the initial state, and it decreases when  $S$  increases, since  $-d\mathcal{W}_{\text{th}}/dS$  is the temperature of the final state reached. However, the situation is different for finite systems. Consider, for instance, a three-level system with eigenenergies  $\varepsilon_{1,3} = \mp 1$ ,  $\varepsilon_2 = 0$ . The eigenstates of  $\rho_0$  and  $\sigma_0$  are taken as  $|r_{1,3}\rangle = |s_{1,3}\rangle = (|\varepsilon_1\rangle \mp |\varepsilon_3\rangle)/\sqrt{2}$ ,  $|r_2\rangle = |s_2\rangle = |\varepsilon_2\rangle$ , so that  $E(\rho_0) = E(\sigma_0) = 0$ . If their eigenvalues are  $\{r_j\} = \{0.90, 0.08, 0.02\}$  and  $\{s_j\} = \{0.91, 0.05, 0.04\}$ , the entropy  $S(\rho_0) \simeq 0.375$  exceeds  $S(\sigma_0) \simeq 0.364$ . Accordingly, the thermodynamic bound  $\mathcal{W}_{\text{th}}(\rho_0) \simeq 0.882$  for the work is smaller than  $\mathcal{W}_{\text{th}}(\sigma_0) \simeq 0.887$ . Nevertheless, the ergotropy  $\mathcal{W}(\rho_0) = 0.88$  of  $\rho_0$  is larger than the ergotropy  $\mathcal{W}(\sigma_0) = 0.87$  of  $\sigma_0$ . The actually reachable bounds are, as expected, lower than the corresponding  $\mathcal{W}_{\text{th}}$ 's, but they are reversed in order: the entropically more disordered state  $\rho_0$  may provide more work.

Thus, the entropy criterion fails for comparing the ergotropies. The theory of majorization<sup>13</sup>, that we briefly recall now, provides another criterion which may be helpful. In quantum statistical mechanics<sup>4,14</sup> a density operator  $\rho$  is said to majorize  $\sigma$  if their eigenvalues  $r_j$  and  $s_j$ , set in the decreasing order (6), satisfy

$$\sum_{j=1}^k r_j \geq \sum_{j=1}^k s_j, \quad \text{for any } k \geq 1. \quad (11)$$

This property, denoted as  $\rho \succ \sigma$ , is transitive ( $\rho \succ \sigma$  and  $\sigma \succ \tau$  imply  $\rho \succ \tau$ ). It characterizes order, but in a stronger way than entropy since  $\rho \succ \sigma$  implies not only  $S(\rho) \leq S(\sigma)$ , but also  $\text{tr} f(\rho) \leq \text{tr} f(\sigma)$  for any concave function  $f(x)$ . Pure states majorize all states, while in a Hilbert space of dimension  $n$  all states majorize  $\rho = 1/n$ . If we have both  $\rho \succ \sigma$  and  $\sigma \succ \rho$ , then  $\rho$  and  $\sigma$  are unitarily equivalent. However, the order defined by majorization is incomplete since, for  $n \geq 3$ , pairs of states  $\rho$  and  $\sigma$  exist of which neither majorizes the other.

Returning to the comparison of the activities of  $\rho_0$  and  $\sigma_0$  with  $E(\rho_0) = E(\sigma_0)$ , we find after summation by parts the ergotropy difference  $\delta\mathcal{W} \equiv \mathcal{W}(\rho_0) - \mathcal{W}(\sigma_0)$  as

$$\delta\mathcal{W} = \sum_{j \geq 1} (s_j - r_j) \varepsilon_j = \sum_{k \geq 1} (\varepsilon_{k+1} - \varepsilon_k) \sum_{j=1}^k (r_j - s_j). \quad (12)$$

Hence a sufficient condition for  $\rho_0$  to be more active than  $\sigma_0$  is  $\rho_0 \succ \sigma_0$  ( $S(\rho_0) \leq S(\sigma_0)$  alone is neither necessary nor sufficient). There exists a wide class of non-unitary evolutions<sup>14</sup> which lead from a state  $\rho_0$  to  $\sigma_0$  such that  $\rho_0 \succ \sigma_0$ . If  $\rho_0$  and  $\sigma_0$  have the same energy, we have  $\mathcal{W}(\rho_0) \leq \mathcal{W}(\sigma_0)$ . For instance, the diagonal part  $\bar{\rho}_0 = \sum_k |\varepsilon_k\rangle \langle \varepsilon_k| \rho_0 |\varepsilon_k\rangle \langle \varepsilon_k|$  of  $\rho_0$  has the same energy as  $\rho_0$  itself, but  $\mathcal{W}(\rho_0) \geq \mathcal{W}(\bar{\rho}_0)$  since  $\rho_0 \succ \bar{\rho}_0$ <sup>13</sup>. In order to find opposite behaviors in the comparison of ergotropies and of free energies (or entropies), we have to search for cases when  $\rho_0 \not\succ \sigma_0$  and  $\rho_0 \not\prec \sigma_0$ . All pairs of inequalities  $\mathcal{W}(\rho_0) \geq \mathcal{W}(\sigma_0)$  and  $S(\rho_0) \geq S(\sigma_0)$  may then occur, as illustrated by examples given above and below.

*Auxiliary system.* If  $S$  is supplemented with an auxiliary system  $\Omega$  with Hamiltonian  $H_\Omega$  and initial state  $\omega_0$ , the overall Hamiltonian  $H + H_\Omega + V(t)$ , where  $V(t)$  couples  $S + \Omega$  with external sources, generates a unitary transformation in the product Hilbert space, which is more general than for work sources coupled separately to  $S$  and  $\Omega$ . The initial state  $\rho_0 \otimes \omega_0$  is uncorrelated and the evolution conserves its (factorized) eigenvalues. The ergotropy satisfies  $\mathcal{W}(\rho_0 \otimes \omega_0) \geq \mathcal{W}(\rho_0) + \mathcal{W}(\omega_0)$ , the same inequality as for  $\mathcal{W}_{\text{th}}$ . Consider, however, again two states  $\rho_0$  and  $\sigma_0$  with the same energy. If they are macroscopic and satisfy  $\mathcal{W}_{\text{th}}(\rho_0) > \mathcal{W}_{\text{th}}(\sigma_0)$ , this ordering of activities is not changed by the introduction of the auxiliary system, since the additivity of entropy for the initial states implies  $\mathcal{W}_{\text{th}}(\rho_0 \otimes \omega_0) > \mathcal{W}_{\text{th}}(\sigma_0 \otimes \omega_0)$ . But for finite systems the order of ergotropies can be reversed. As a first example consider for  $S$  the same three-level system as above, with eigenvalues of  $\rho_0$  and  $\sigma_0$  now equal to  $\{r_j\} = \{0.8, 0.1, 0.1\}$  and  $\{s_j\} = \{0.5, 0.5, 0\}$ . For  $\Omega$  we take a two-level system with eigenenergies 0 and  $\Delta > 0$ , initially in a pure state. Although  $\rho_0 \neq \sigma_0$ , we have both  $S(\rho_0) \simeq 0.639 < S(\sigma_0) \simeq 0.693$  and  $\mathcal{W}(\rho_0) = 0.7 > \mathcal{W}(\sigma_0) = 0.5$ . However, coupling with  $\Omega$ , which does not change the entropies, reverses the inequality for the ergotropies if  $\Delta < 1/4$ , since (for  $\Delta < 1$ )  $\mathcal{W}(\rho_0 \otimes \omega_0) - \mathcal{W}(\sigma_0 \otimes \omega_0) = 0.4\Delta - 0.1$ . For  $\Delta = 0$ , the auxiliary system  $\Omega$  does not contribute to the energy balance but nevertheless raises  $\mathcal{W}$  owing to its order.

The opposite situation is also possible, provided  $S$  has at least four levels. Consider for instance a system  $S$  with eigenenergies  $\varepsilon_{1,4} = \mp 1$ ,  $\varepsilon_{2,3} = \mp(1-x)$ , with  $0 < x < 1$ . As eigenstates of  $\rho_0$  and  $\sigma_0$  we take  $|r_{1,4}\rangle = |s_{1,4}\rangle = (|\varepsilon_1\rangle \pm |\varepsilon_4\rangle)/\sqrt{2}$ ,  $|r_{2,3}\rangle = |s_{2,3}\rangle = (|\varepsilon_2\rangle \pm |\varepsilon_3\rangle)/\sqrt{2}$ , which ensures  $E(\rho_0) = E(\sigma_0) = 0$ , and as eigenvalues:

$$\{r_j\} = \frac{1}{(1+w)^2} \left\{ w(w+3), \frac{1-w}{2}, \frac{1-w}{2}, 0 \right\}, \quad (13)$$

$$\{s_j\} = \frac{1}{(1+w)^2} \{2w, 2w, w(1-w)^2, (1-w)^3\}, \quad (14)$$

which are ordered according to (6) provided  $1 > w > 1/2$ . The fact that  $\rho_0 \neq \sigma_0$  and  $\sigma_0 \neq \rho_0$  allows to violate the thermodynamical ordering, since we have simultaneously  $S(\rho_0) < S(\sigma_0)$  and  $\mathcal{W}(\rho_0) < \mathcal{W}(\sigma_0)$  for sufficiently small  $x$ , as seen from  $(1+w)^2 [\mathcal{W}(\sigma_0) - \mathcal{W}(\rho_0)] = (1-w)(2w-1) - xw(1+2w-w^2)$ . Take  $\Omega$  as a two-level system; its only relevant feature will be the eigenvalues  $\{w, 1-w\}$  of its initial state  $\omega_0$ . Provided  $1/4 < w^2 < 1/2$ , the equations (11) for  $k = 1, 2, \dots, 8$  are satisfied and hence  $\rho_0 \otimes \omega_0 \succ \sigma_0 \otimes \omega_0$ . This implies  $\mathcal{W}(\rho_0 \otimes \omega_0) > \mathcal{W}(\sigma_0 \otimes \omega_0)$ :  $\Omega$  restores for the ergotropies the order inferred from the thermodynamic relation  $S(\rho_0) < S(\sigma_0)$ .

All these contradictions between the predictions of thermodynamics and the behavior of finite systems do not occur for the subset of states that may be ordered in the sense of majorization: then  $\rho_0 \succ \sigma_0$  implies both  $S(\rho_0) \leq S(\sigma_0)$  and  $\mathcal{W}(\rho_0) \geq \mathcal{W}(\sigma_0)$  and  $\mathcal{W}(\rho_0 \otimes \omega_0) \geq \mathcal{W}(\sigma_0 \otimes \omega_0)$  for an arbitrary  $\omega_0$ .

*Correlations.* In the above examples the initial state of  $S+\Omega$  was uncorrelated, but not the final state, because evolution permutes its eigenvectors although its eigenvalues remain factorized. Thus, contrary to thermodynamic intuition, the maximum work can be achieved owing to creation of correlations.

Conversely, if the initial state  $Q_0$  of  $S+\Omega$  is correlated, thermodynamics predicts that the available work is increased, due to the subadditivity of entropy,  $S(Q_0) \leq S(\rho_0) + S(\sigma_0)$ , where  $\rho_0 = \text{tr}_\Omega Q_0$  and  $\sigma_0 = \text{tr}_S Q_0$  are the marginal states of  $S$  and  $\Omega$ , respectively. However, for finite quantum systems, we have to compare the ergotropies  $\mathcal{W}(Q_0)$  and  $\mathcal{W}(\rho_0 \otimes \sigma_0)$ . Take for  $S$  a system with three energy levels  $\varepsilon_i$ ,  $i = 1, 2, 3$  and for  $\Omega$  a two-level system  $k = 1, 2$  with energy levels  $0, \varepsilon$  such that  $0 < \varepsilon < \varepsilon_2 - \varepsilon_1$ ,  $\varepsilon < \varepsilon_3 - \varepsilon_2$ , and for  $S + \Omega$  a stationary initial state  $Q_0$ . Denoting the common eigenstates of  $H + H_\Omega$  and  $Q_0$  as  $|i, k\rangle$ , we assume that the eigenvalues  $q_{ik}$  of  $Q_0$  are ordered as  $q_{11} > q_{12} > q_{21} > q_{22} > q_{31} > q_{32}$ . Then  $Q_0$  is both correlated and passive. Suppressing correlations leads to a factorized state  $\rho_0 \otimes \omega_0$  with the same energy, and eigenvalues  $r_i = \sum_{k=1}^2 q_{ik}$  for  $\rho_0$  and  $p_k = \sum_{i=1}^3 q_{ik}$  for  $\omega_0$ . The ordering of the set  $r_i p_k$  may now differ from that of  $q_{ik}$ ; for instance, if  $q_{11}$  is close to one and all other  $q_{ik}$ 's are small with the same order of magnitude, we have  $r_2 p_2 < r_3 p_1$ , and  $\mathcal{W}(\rho_0 \otimes \omega_0) = (\varepsilon_3 - \varepsilon_2 - \varepsilon)(r_3 p_1 - r_2 p_2) > 0$ . Suppressing the correlations has thus let the system  $S + \Omega$  become active. Altogether, the order carried by correlations, although it manifests itself directly in the entropy, has no relation with increase or decrease of ergotropy.

*Fluctuations of work.* The work  $-W$  extracted from  $S$  by means of external sources acting in a cycle was defined by (2) as the expectation value of the difference between the initial and final energies of  $S$ . This expectation value can also be observed as an average<sup>11</sup> by coupling the macroscopic sources of work to  $N \gg 1$  identical systems  $S$  operating in parallel, in such a way that their total Hamiltonian is the sum of the Hamiltonians  $H + V(t)$  of each one. However, for a single system  $S$ , the work is expected to fluctuate. In order to evaluate such fluctuations, we need to define work as a random variable for the dynamics described by the optimal unitary transformation (9). To do this, we need to determine, for each single realization in the statistical ensemble described by  $\rho_0$ , the initial and final energy of  $S$ . This can be done unambiguously, without perturbing the overall ensemble  $\rho_0$ , only if both  $\rho_0$  and  $\rho(\tau)$  commute with  $H$ . Then the measurement of energy at the time  $t = 0$  allows to filter systems which have the same initial energy  $\varepsilon_k^{(i)}$  after the measurement. The evolution operator (9) then determines for each initial  $\varepsilon_k^{(i)}$  the final energy  $\varepsilon_l^{(f)}$ , hence the work  $\varepsilon_k^{(i)} - \varepsilon_l^{(f)}$  is given by  $S$  to the sources. We can thus regard

$\varepsilon_k^{(i)} - \varepsilon_l^{(f)}$  as a *classical* random variable describing work, and governed by the diagonal elements  $r_j$  of the density matrix  $\rho_0$ . In the same way as  $\mathcal{W} = \sum_{jk} r_j P_{jk}(\varepsilon_k - \varepsilon_j)$ , where  $P_{jk} = |\langle \varepsilon_j | U | \varepsilon_k \rangle|^2$  is a permutation matrix, we get the *ergotropy dispersion*:

$$\Delta \mathcal{W}^2 = \sum_{jk} r_j P_{jk}(\varepsilon_k - \varepsilon_j)^2 - \mathcal{W}^2. \quad (15)$$

It vanishes for passive states, for which  $P_{jk} = \delta_{jk}$  and  $\mathcal{W} \equiv \max W = 0$ : one cannot hope to put no work in average, and get some work out by making use of fluctuations. For active states,  $\Delta \mathcal{W}$  may become sizeable. In the example of a two level-system with the initial state:  $\rho_0 = r_1 |\varepsilon_2\rangle\langle\varepsilon_2| + r_2 |\varepsilon_1\rangle\langle\varepsilon_1|$ , the ergotropy is  $\mathcal{W} = (r_1 - r_2)(\varepsilon_2 - \varepsilon_1)$  and its fluctuation from (15) is  $\Delta \mathcal{W} = 2\sqrt{r_1 r_2}(\varepsilon_2 - \varepsilon_1)$ . The relative fluctuation  $\Delta \mathcal{W}/\mathcal{W}$  vanishes for  $r_1 = 1$ ,  $r_2 = 0$ , when  $\mathcal{W}$  is largest; it becomes large when  $\mathcal{W}$  is small, i.e.,  $r_1 \rightarrow r_2 \rightarrow \frac{1}{2}$ . Many systems  $S$  should then operate in parallel to produce on average the amount  $\mathcal{W}$  in a predictable fashion.

*Conclusion.* Maximal work extraction is one of the basic problems of thermodynamics and has applications in various processes of energy conversion<sup>1,2,6</sup>. In macroscopic physics, the answer (4) is governed by the non-decrease of entropy. We have shown that finite devices are less efficient in this respect: any evolution of a thermally (but not mechanically) isolated quantum system must leave unchanged not only this entropy, but all the eigenvalues of the density operator, which prevents in most situations the thermodynamic bound from being attainable. We have given a general explicit expression (8) for the “ergotropy”, the quantity which, for finite systems, replaces the free energy: it is the upper bound of the work that a finite system  $S$  in a non-equilibrium initial state  $\rho_0$  may yield if it is coupled to external sources of work undergoing a cyclic transformation. Many interaction Hamiltonians  $V(t)$  allow to reach this bound.

The proper measure of order for comparing the abilities of work production of finite systems is thus ergotropy and not free energy. Several consequences of this result contradict thermodynamic intuition. Consider, for instance, a state  $\sigma_0$  of  $S$  having the same energy as  $\rho_0$  and lower entropy. Thermodynamics suggests that more work might be extracted from  $\sigma_0$  than from  $\rho_0$ , and moreover that the presence of an auxiliary system  $\Omega$ , in a state  $\omega_0$  initially uncorrelated with  $S$ , preserves this property. Such statements can be violated in finite quantum systems. However, even for finite systems, there is a domain of states defined by the majorization relation, where predictions of thermodynamics are qualitatively correct.

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