

Catalysis of heat-to-work conversion in quantum machines

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We propose a hitherto-unexplored concept in quantum thermodynamics: catalysis of heat-to-work conversion by quantum nonlinear pumping of the piston mode which extracts work from the machine. This concept is analogous to chemical reaction catalysis: Small energy investment by the catalyst (pump) may yield a large increase in heat-to-work conversion. Since it is powered by thermal baths, the catalyzed machine adheres to the Carnot bound, but may strongly enhance its efficiency and power compared with its noncatalyzed counterparts. This enhancement stems from the increased ability of the squeezed piston to store work. Remarkably, the fraction of piston energy that is convertible into work may then approach unity. The present machine and its counterparts powered by squeezed baths share a common feature: Neither is a genuine heat engine. However, a squeezed pump that catalyzes heat-to-work conversion by small investment of work is much more advantageous than a squeezed bath that simply transduces part of the work invested in its squeezing into work performed by the machine.

quantum machines | quantum thermodynamics | squeezing | Carnot efficiency | quantum catalysis

The intimate rapport of thermodynamics with the theory of open quantum systems and its applications to quantum heat engines has been long and fruitful. The landmarks of this rapport have been Einstein's theory of spontaneous and stimulated emission (1), the determination of maser efficiency (2–4), and its extension to the micromaser (5). Among the diverse proposals for quantum heat engines (6–35), intriguing suggestions have been made to boost the Carnot efficiency through bath preparation in nonthermal [population-inverted (29), phase-coherent (phaseonium) (30), or squeezed (31, 35)] states.

However, quantum machines fueled by such nonthermal baths adhere to rules that differ from those of quantum heat engines (32, 33, 36) (*Discussion*). Here, instead, we restrict ourselves to machines fueled by thermal baths, but introduce the concept of catalysis known from the theory of chemical reaction (37), whereby a small amount of catalyst (here, a weak pump) strongly enhances the reaction rate (here, the heat-to-work conversion).

We illustrate this concept for the minimal model (18, 20, 34) of a fully quantized heat machine wherein a two-level system (TLS) acts as the working fluid (WF) that simultaneously interacts with hot and cold baths and is dispersively (off-resonantly) coupled to a piston mode that undergoes amplification and extracts work. This model is here extended by subjecting the quantized piston mode to nonlinear (quadratic) pumping. Our motivation for considering this scheme is that nonlinearly pumped parametric amplifiers may produce squeezed output (38–42). We wish to find out whether this property may catalyze the machine performance. To this end, we investigate work extraction by combining quantum-optical amplification and dissipation theory (38–41) with thermodynamics (43).

Our main insight is that the quadratic pumping (5) of the piston mode provides a powerful handle on the performance of

the machine, which is determined by the piston state nonpassivity (43–50): the capacity of the piston state to store work. In analogy to the potential energy stored in a classical (mechanical) device or the charging energy of a battery, nonpassivity [also known as ergotropy (48)] is a unique measure of work extractable from a quantum state. We find that under quadratic pumping, the piston mode evolves into a thermal-squeezed state that strongly enhances its work capacity (nonpassivity) compared with its linearly pumped or unpumped counterparts. The resulting catalysis effects are that the output power and efficiency of heat-to-work conversion are drastically enhanced, and the piston “charging efficiency” (i.e., the fraction of piston energy convertible to work) may approach unity. On the other hand, since the machine is fueled by thermal baths, the Carnot efficiency bound remains valid upon subtracting the work invested by the pump, so that the machine abides by the first and second laws of thermodynamics (51).

The Model and Basic Assumptions

In our illustration of catalysis for a quantum heat-powered engine, the WF is composed of a TLS, S , which is dissipatively coupled to two thermal baths all the time. S is off-resonantly coupled to a pumped harmonic oscillator, dubbed a piston, P , which can collect and store the extracted work. The cold and hot baths, denoted by C and H , respectively, are “spectrally nonoverlapping,” as detailed below. P is not coupled to its own bath to avoid energy dissipation, which would disturb the thermodynamical balance of heat and work in the total system.

The Hamiltonian has the form ($\hbar = 1$ in the following):

Significance

The traditional (19th century) rules of thermodynamics were conceived for engines that convert heat into work. Recently, these rules have been scrutinized, assuming that the engines have quantum properties, but we still have no complete answer to the question: Are these rules then the same as the traditional ones? Here, we subject a “piston”—an oscillator that extracts work from the engine—to energy “pumping” that renders this oscillator quantum and nonlinear. We show that even weak pumping may strongly catalyze the heat-to-work conversion rate. This catalysis, analogous to its chemical-reaction counterpart, is a manifestation of “quantumness” in heat engines, yet it adheres to the traditional laws of thermodynamics.

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$$H_{tot} = H_{pump}(t) + H_{S+P} + \sum_{j=H,C} (H_{SB}^j + H_B^j); \quad [1]$$

$$H_{S+P} = H_S + H_P + H_{SP},$$

$$H_S = \frac{1}{2}\omega_0\sigma_Z; H_P = \nu a^\dagger a; H_{SP} = g\sigma_Z \otimes (a + a^\dagger), \quad [2]$$

where g is a real coefficient characterizing the strength of the coupling between S and P . Here, $H_{pump}(t)$ denotes the pumping of P (described below); S and P are “off-resonantly (dispersively) coupled” (52–55), g being the coupling strength and a (σ_-), a^\dagger (σ_+), respectively, the P -mode (S -system) annihilation (lowering) and creation (raising) operators. The last term of Eq. 1 is

$$H_B^j = (B^\dagger B)_{jj}; \quad H_{SB}^j = \sigma_X B_j, \quad [3]$$

where H_B^j is the (multimode) free Hamiltonian of the bath $j = H, C$; H_{SB}^j being the coupling Hamiltonian between the j -th bath and the X -spinor (σ_X) of S . The direct interaction of S with the two baths forces S to be in a periodic steady state (10). By contrast, the P mode is isolated from the baths, yet the baths change its energy and entropy indirectly via S (Fig. 1). Namely, the state of the piston must inevitably keep changing and cannot be fully cyclic.

The key feature we consider in Eq. 1 is the coupling of the quantized piston to an external pumping Hamiltonian

$$H_{pump}(t) = \frac{i}{2}[\kappa e^{-2i\nu t} a^{\dagger 2} - \kappa^* e^{2i\nu t} a^2], \quad [4]$$

$|\kappa|$ being the undepleted (classical) pumping rate of this (degenerate) parametric amplifier (5) whose quadratic form generates squeezing (5, 38, 40) and $\phi := \arg \kappa$ corresponds to the phase of

the (classical) pump field (SI Text), which oscillates at frequency 2ν , twice as fast as the cavity field. Both pump and cavity field may be obtained, through a beam splitter, from a classical field with phase $\phi/2$, the cavity field resulting from the injection into the cavity mode of one of the outputs of the beam splitter, while the parametric amplifier is pumped by the other output, after undergoing a frequency doubling process. This assures the possibility of controlling the relative phase between the pump and the cavity field. It will be shown that, if the initial state of the field in the cavity is thermal, the final results do not depend on ϕ . On the other hand, if the cavity field is initially in a coherent state, the result depends only on the relative phase between the incoming classical field and the coherent state. At the steady state for S , the work output of P is not only modified by the pumping, but is also amplified on account of the system–bath coupling. In what follows, we show that the two processes are nonadditive and may reinforce each other. This nonadditivity is essential for the catalysis effects discussed here.

A cavity-based nonlinear parametric amplifier (5, 38) coupled to two heat baths with different temperatures and spectra can realize the present model (Fig. 1A). The intracavity WF of the machine may be an atomic gas (56), an optomechanical setup (57), or a collection of superconducting flux qubits (53–55). The SP coupling in Eq. 2 is experimentally realizable by a flux qubit which is dispersively coupled to high- Q (phonon) mode of a nanomechanical cavity (cantilever) that acts as the P mode (53, 58). Alternatively, P can be a field mode of a coplanar resonator whose quantized electromagnetic field quadrature $a + a^\dagger$ affects the flux qubit energy σ_Z (15, 54, 55).

Outline of the Dynamical Analysis

The dynamics of such pumped quantum open systems, consistent with the laws of thermodynamics, is given in terms of the Floquet expansion (18, 20, 34, 43) of the Lindblad (Markovian) equations (59), which involves the bath response at the H_{S+P} Hamiltonian eigenvalues: the resonant frequencies ω_0 (of S) and ν (of P) and combination frequencies ($\omega_\pm = \omega_0 \pm \nu$) thereof. To investigate the dependence of work on the state of P , we let S reach its steady state and treat the pumping as a weak perturbation causing much slower changes than the free-evolution periods ω_0^{-1} and ν^{-1} .

The Lindblad master equation for the piston mode $\rho_P = Tr_{S+P} \rho_{S+P}$ is then expressed in terms of a Fokker–Planck (FP) equation for the slowly changing piston. Its drift (amplification) and diffusion (thermalization) rates, Γ and D respectively, depend on the sum of the cold- and hot-bath response spectra $G(\omega) = \sum_{j=H,C} G_j(\omega)$, sampled at the combination frequencies for the S – P coupling Hamiltonian H_{SP} (SI Text).

Work extraction requires $\Gamma < 0$ (gain). One must necessarily have $D \geq |\Gamma|$ (SI Text), with small ratio $D/|\Gamma|$ being preferred, so that the piston thermalization induced by diffusion sets in as slowly as possible. The pumping rate $|\kappa|$ is set to be much smaller than both $|\Gamma|$ and D (under the weak-pumping condition), which are in turn much smaller than the frequencies ν and ω_0 (under the weak system–bath coupling condition). Under these conditions, $\langle H_P(t) \rangle$ undergoes quasicyclic, slowly amplifying evolution. It is also assumed that the ratio between the system–piston coupling g and the frequency ν is small. Then, the resulting master equation for the P mode (SI Text) can be simplified.

The corresponding FP equation for the quantized P may be solved analytically (60) for an initial Gaussian state, $\rho_P(0)$, under quadratic pumping that generates squeezing. The corresponding Wigner distribution then evolves in the amplification (gain) regime $\Gamma < 0$ toward a nonpassive distribution (SI Text) in the form of a 2D Gaussian with maximal and minimal widths f_1 and f_2 (Eq. 11) along the respective orthogonal axes x_1 and x_2 determined by the phase of the pump (SI Text). The width f_1 grows much faster than f_2 (Fig. 1B), causing squeezing.

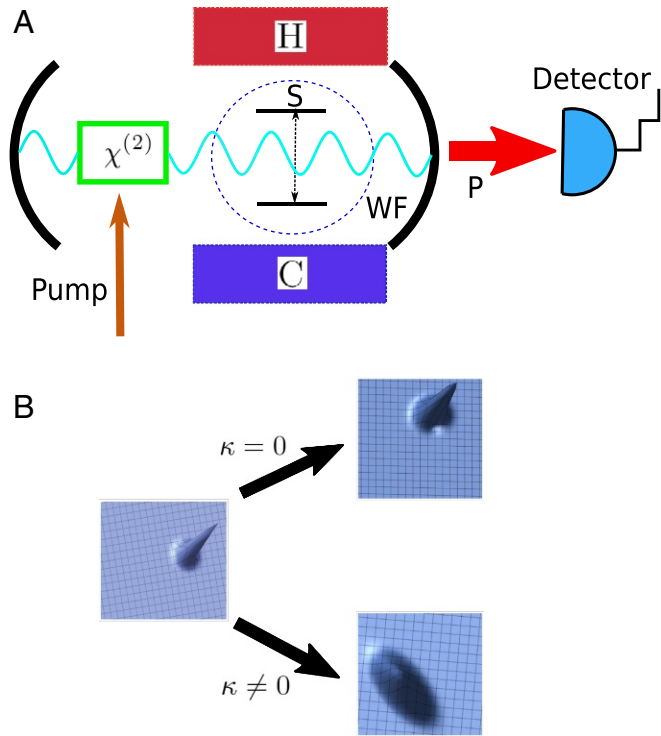


Fig. 1. (A) A schematic diagram of a cavity-based quantized heat engine with quadratically pumped (via a $\chi^{(2)}$ nonlinear medium) piston P and a TLS S as WF. The hot (H) and cold (C) baths are in contact with the WF. (B) The evolution of the Wigner phase-plane distribution function of an initial coherent state into a 2D Gaussian with two different quadrature widths compared with the unpumped case shows that the nonlinear pump enhances the nonpassivity (ergotropy).

Work Extraction

To evaluate work extraction by P at the steady state of S, we take into account the pumping in the energy balance according to the first law of thermodynamics (10, 43, 51).

$$d\langle H_P \rangle = dQ_{P/H} + dQ_{P/C} + dW_{pump}, \quad [5]$$

where the *l.h.s* is the infinitesimal change in mean energy of the pumped piston and $dQ_{P/H(C)}$ are the infinitesimal amounts of heat supplied by H or C to P, respectively. Importantly, dW_{pump} is the energy supply by the pump mode to the piston: Because of their coherent (isentropic) interaction, this energy is pure work, without heat transfer from the pump to the piston.

Work Efficiency Bound for Pumped Piston

For a given ρ_P , the maximum extractable work (15, 43–45, 50) is expressed by

$$W_{Max}(\rho_P) = \langle H_P(\rho_P) \rangle - \langle H_P(\rho_P^{pas}) \rangle \quad [6]$$

where ρ_P^{pas} is a passive state (43–50), defined as the state with the least energy that is unitarily accessible from ρ_P . No work (ergotropy) can be extracted from a passive state, $W_{Max}(\rho_P^{pas}) = 0$. The signature of a passive state is that its probability distribution falls off monotonically as the energy increases, and any nonmonotonicity renders it nonpassive. For example, every population-inverted state is nonpassive, and so are, e.g., coherent (except vacuum) or squeezed field states, whereas thermal states are passive.

For Gaussian states (used here), the passive state ρ_P^{pas} related to ρ_P is a Gibbs state (61): a minimal-energy state with the same entropy as ρ_P . This Gibbs state has the form

$$\rho_P^{pas}(t) = Z^{-1} e^{-\frac{H_P}{T_P(t)}} \quad [7]$$

with an evolving temperature $T_P(t)$. Upon taking the time derivative Eq. 6 and using Eq. 7, we find

$$\dot{P}_{Max} = \langle \dot{H}_P \rangle - T_P(t) \dot{S}_P(t) - \dot{W}_{pump}. \quad [8]$$

Here we have subtracted the power supplied by the pumping since it should not be included in the heat-to-work conversion balance, so that Eq. 8 is the net rate of extractable work converted from heat. The first term $\langle \dot{H}_P \rangle$ is the ideal power obtained from heat under perfect nonpassivity. The second term $-T_P(t) \dot{S}_P$ in Eq. 8, reflects the rise with time of the temperature $T_P(t)$ and the entropy production (20) S_P of P: It expresses its passivity increase (or nonpassivity loss).

We note the following fundamental difference between the present machine and a usual heat engine. The usual power (or rate of work) is given by $\langle \dot{H}_P \rangle$ minus the incoming heat flow. Here, however, the rate of extractable work is given by $\langle \dot{H}_P \rangle$ minus the passivity increase. A natural question arising from this observation is: How does the pumping affect the machine performance? To answer this question, we henceforth consider the limit $\dot{W}_{pump} \ll \dot{W}_{Max}$, $\dot{Q}_{P/H}$ (given in SI Text) wherein the machine is approximately a heat engine. It therefore must abide by the second law and the ensuing Carnot bound. However, as we show, its performance may be strongly catalyzed by the pump squeezing, a surprising and hitherto-unexplored effect.

To obtain better insight into the catalytic nature of nonlinear pumping in this setup, we compute the thermodynamic engine efficiency, which is defined as the ratio of the net work (or power) output to the heat input supplied by H to SP (or its rate, denoted by $\dot{Q}_{SP/H}$)

$$\eta = \frac{\dot{W}_{Max} - \dot{W}_{pump}}{\dot{Q}_{SP/H}}. \quad [9]$$

The maximal extractable work W_{Max} exponentially increases under gain ($\Gamma < 0$) before saturation sets in. Explicitly, the effi-

ciency can be calculated (SI Text) for any Gaussian states in terms of $n_{pas}(t)$, the mean number of passive quanta corresponding to $T_P(t)$ (and related to the passivity increase through $\dot{n}_{pas} = T_P(t) \dot{S}_P(t)/\nu$), the evolving squeezing parameter $r(t)$ (62, 63) of P, and the expectation values x_{10} , x_{20} , of the quadratures operators \hat{x}_1 and \hat{x}_2 (defined in SI Text) taken with respect to the initial state of P. Only thermal states can be considered as “natural” initial states. For such states, $x_{10} = x_{20} = 0$, and the energy of P as well as the extractable work do not depend on ϕ . By contrast, any nonthermal features of the initial state of P, such as squeezing or displacement (in phase-space), result from “artificial” state engineering or preparation. Such engineering/preparation demands additional work input and thus modifies the global work balance; hence, the preparation cost must be accounted for. One should note that, for initial coherent states (where $x_{10}, x_{20} \neq 0$), the energy of P depends on the relative phase between the incoming classical field and the coherent state (SI Text), well defined as long as the same pump beam is used for the parametric amplifier and for the preparation of the initial coherent state.

Keeping those observations in mind, we derive in SI Text the expressions of the passivity increase and $\dot{Q}_{SP/H}$ for initial Gaussian states. Both quantities are enhanced by the pumping. Surprisingly, the heat flow $\dot{Q}_{SP/H}$ is more strongly enhanced, which yields an ergotropy increase together with an efficiency increase. Assuming that $n_{pas}(t) \gg D/|\Gamma|$, the efficiency can be simplified to (SI Text)

$$\eta \simeq \frac{\nu}{\omega_+} \left[1 - \frac{n_{pas} + 1/2}{(n_{pas} + \frac{1}{2}) \cosh 2r(t) + x_{10}^2 e^{2\Gamma+t} + x_{20}^2 e^{2\Gamma-t}} \right], \quad [10]$$

where $\Gamma_{\pm} = -\Gamma/2 \pm |\kappa|$. The squeezing parameter is given by the relation (62, 63) $\cosh 2r(t) = (f_1 + f_2)/[n_{pas}(t) + 1/2]$, where f_1 and f_2 are, respectively, the maximal and minimal width of the Wigner distribution (SI Text),

$$f_{1,2} = \frac{2n_{pas}(0) + 1}{4} e^{2\Gamma_{\pm}t} + \frac{(D + \frac{\Gamma}{2})}{4\Gamma_{\pm}} (e^{2\Gamma_{\pm}t} - 1), \quad [11]$$

where $n_{pas}(0)$ denotes the initial number of passive quanta or thermal excitation, the above expression of $f_{1,2}$ being valid for initially unsqueezed states (the general situation is discussed in SI Text). The number of passive quanta can be expressed in terms of the widths f_1 and f_2 (62, 63) and for initially unsqueezed states is reduced to $n_{pas}(t) = 2\sqrt{f_1 f_2} - 1/2$. Then, the second term inside the brackets in Eq. 10 can be rewritten as $2\sqrt{f_1 f_2}/[f_1 + f_2 + x_{10}^2 e^{2\Gamma_{+}t} + x_{20}^2 e^{2\Gamma_{-}t}]$. Since the sum $f_1 + f_2$ rises in time faster than $\sqrt{f_1 f_2}$, the efficiency reaches the maximal attainable efficiency η_{Max} (even when $x_{10} = x_{20} = 0$), bounded by the Carnot efficiency (SI Text),

$$\eta \xrightarrow[t \geq |\kappa|^{-1}]{} \eta_{Max} := \frac{\nu}{\omega_+} \leq \eta_{Carnot} = 1 - \frac{T_C}{T_H}. \quad [12]$$

As usual, the Carnot efficiency is obtained in the zero power limit (Fig. 2B) that corresponds to setting $T_C/T_H = \omega_0/\omega_+$ (SI Text). The above result remains valid for arbitrary initial Gaussian states, although the general expressions (detailed in SI Text) are more involved.

By contrast, for linear pumping or in the absence of any pumping ($\kappa = r(t) = 0$), the passivity term that limits the work (in Eq. 6) or the power (in Eq. 8) becomes small only in the semiclassical limit (when $x_{10}^2 + x_{20}^2 = |\alpha_0|^2 \gg 1$ provided the weak coupling approximation $(g/\nu)|\alpha_0| \ll 1$ still holds). The efficiency expression in the linearly pumped gain regime ($\Gamma < 0$) is then (SI Text)

$$\eta_L = \frac{\nu}{\omega_+} \frac{|\alpha(t)|^2}{|\alpha(t)|^2 + n_{pas}(t) + D/|\Gamma|}, \quad [13]$$

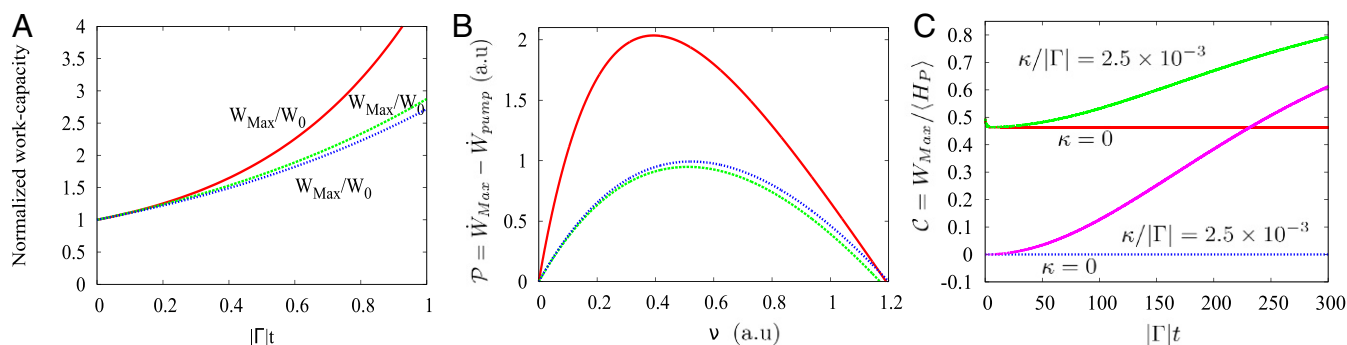


Fig. 2. (A) Maximal work capacity (charge) drastically increases in the presence of nonlinear pumping (red) compared with its unpumped (blue) and linear (green) counterparts (normalized by the initial work capacity W_0) as a function of $|\Gamma|t$ for an initial coherent state with $\langle n_P(0) \rangle = 1$. (B) The power output as a function of piston frequency in arbitrary units (a.u.) for nonlinearly pumped (red), linearly pumped (blue), and unpumped counterparts (green). The endpoint corresponds to maximal efficiency with zero power for the parameter set $\omega_0/\omega_+ = T_C/T_H = 0.6$; $\omega_0 = 1.8$ (a.u.). In both A and B, the phase is chosen as $\phi = \pi/4$, and the plot of the work capacity for linear pumping is obtained from the exact expression in *SI Text*. (C) The charging efficiency (the ratio between maximum extractable work and the energy stored in the piston) approaches unity even for weak nonlinear pumping ($|\kappa| \ll |\Gamma|$) and differs drastically (green, coherent; pink, thermal) from the $\kappa = 0$ case (red, coherent; blue, thermal).

where $\alpha(t)$ is the complex displacement (in phase-space) generated by the linear coupling dynamics. The displacement $|\alpha(t)|$ grows at the same rate as the passivity $n_{pas}(t)$, so that η_L remains very limited and does not reach η_{max} (*SI Text*). Without any pump, the efficiency is reduced to

$$\eta_0 = \frac{\nu}{\omega_+} \left[\frac{|\alpha_0|^2}{|\alpha_0|^2 + n_{pas}(0) + D/|\Gamma|} \right]. \quad [14]$$

This expression shows that the catalytic effect of linear pumping (i.e., the difference between Eqs. 13 and 14) is very small (*SI Text*).

To maximize the efficiency in Eqs. 13 and 14, n_{pas} must be minimized while the coherent nonpassive $|\alpha(t)|^2$ must be maximized. A comparison between the efficiency in the unpumped [14], linearly pumped [13], and nonlinearly pumped [10, 12] situations reveals that quadratic pumping may dramatically enhance the maximal work capacity, as shown in Fig. 24 for a small initial piston charging $\langle n_P(0) \rangle \sim 1$, even if the piston is initially in a thermal (passive) state. When the nonlinear pumping is on, the energy increase due to the heat input is amplified by the squeezing as $\nu(n_{pas}(t) + 1/2) \cosh 2r(t)$ (*SI Text*). However, the passive energy remains equal to $\nu n_{pas}(t)$, as it is unaffected by the squeezing. As a consequence of the nonadditive character of the passive and nonpassive energies, any heat input results in an ergotropy (extractable work) increase. Hence, the stronger the squeezing, the higher the efficiency. To complete this picture, we have to take into account the effect of the baths on the squeezing parameter (*SI Text*).

By contrast, linear pumping generates an energy contribution which is independent of thermal energy, so that the passive and nonpassive contributions remain additive $\nu n_{pas}(t) + \nu |\alpha(t)|^2$ (*SI Text*). Consequently, the ergotropy increase generated by heat input is then very limited (Fig. 2, Fig. S1, and *SI Text*). Note that, for any pumping, the fundamental requirement is $\Gamma < 0$, i.e., positive gain induced by the bath.

Importantly, the charging efficiency, i.e., the ratio between maximum useful work and the total energy stored in the piston, is enhanced

$$\mathcal{C} = \frac{W_{Max}}{\langle H_P \rangle} \xrightarrow{t \gg |\kappa|^{-1}} 1 \quad [15]$$

under quadratic pumping. The charging efficiency is here proposed as a useful measure of the performance of fully quantized heat machines: The maximum useful work W_{Max} corresponds to the fraction of the piston energy $\langle H_P \rangle$ which can be extracted by a unitary operation (49). Fig. 2C illustrates that quadratic pump-

ing may drastically enhance both work extraction and charging efficiency in the quantized P mode, compared with its unpumped counterpart.

Discussion

Here we set out to explore: Does the fact that a quantum machine is fueled by a heat bath imply that the machine conforms to the traditional rules of thermal (heat) engines? Conversely, does the quantumness of parts of a thermal machine endow it with unique resources? To answer these questions, we have derived the efficiency of a heat-fueled machine whose quantized piston is subject to quadratic pumping. It reveals the possibility of strong catalysis of heat-to-work conversion.

It is instructive to compare the present machine with machines powered by certain nonthermal baths, such as a squeezed-thermal or coherently displaced thermal bath, which render the WF steady state nonpassive (31–33). The Carnot bound may nominally be surpassed in such machines at the expense of work supplied by the bath, but the comparison of their efficiency bound with the Carnot bound of heat machines is inappropriate, because this is imposed by the second law only on heat imparted by the bath. Such nonthermal machines do not adhere to the rules of a heat engine, since they receive both work and heat from

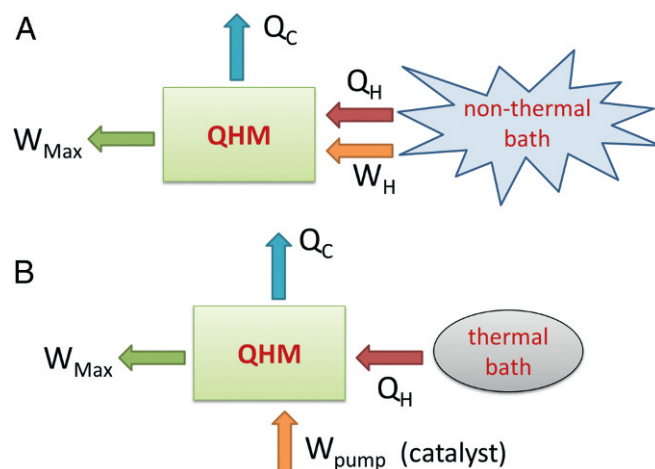


Fig. 3. (A) Scheme of squeezed (nonthermal) bath machine (31–33). (B) Scheme of the present (catalyzed) machine.

external sources (32). Namely, the ability to attain super-Carnot efficiency is an effect of work transferred from the nonthermal bath to the WF (Fig. 3A).

By contrast, in the present setup (Fig. 3B), work supplied by the pump to the piston, thereby squeezing it and rendering it nonpassive, is a catalyst: It allows for strongly enhanced heat-to-work conversion efficiency. The Carnot bound does limit this heat-to-work conversion efficiency because the work contribution from the pumping or piston state preparation is subtracted, the only net energy input being the hot bath.

Another important difference between the two kinds of machines is that in our scheme, the work invested is recovered in the internal energy of P, whereas in a machine where a squeezed thermal bath is used, most of the work invested in squeezing the bath is lost in the bath since only a small part of it is transferred to the WF (36).

Our scheme is also convenient from an experimental point of view since it is much easier to squeeze a single-mode harmonic oscillator (piston) than a bath. A micromaser fed by two-atom clusters (16, 64–67) prepared in nearly equal superposition of doubly excited and doubly unexcited states may also strongly squeeze a cavity-field piston coupled to two heat baths (33).

Cyclic cavity-mirror shaking is another squeezing mechanism (68). The nonpassivity of the output may be verified by homodyning the piston with a local oscillator (5).

In the present work, we consider a WF comprising a single TLS or a dilute sample thereof, with less than one TLS per cubic wavelength, such that collective effects are negligible (69). It would be worth investigating further potential beneficial collective effects (70) in presence of multiple TLSs.

To conclude, the hitherto-unexplored heat-to-work conversion catalysis has been shown to arise from the ability of pump-induced nonlinear (squeezed) piston dynamics to increase and sustain its nonpassivity and thereby its capacity to convert heat to work. Thus, squeezing may provide a uniquely advantageous resource to thermal machines.

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- Einstein A (1916) Emission and absorption of radiation according to the quantum theory. *Verh Dtsch Phys Ges* 18:318–323.
- Scovil HED, Schulz-DuBois EO (1959) Three-level masers as heat engines. *Phys Rev Lett* 2:262–263.
- Geusic JE, Schulz-DuBois EO, De Grasse RW, Scovil HED (1959) Three level spin refrigeration and maser action at 1500 mc/sec. *J Appl Phys* 30:1113–1114.
- Geusic JE, Schulz-DuBois EO, Scovil HED (1967) Quantum equivalent of the Carnot cycle. *Phys Rev* 156:343–351.
- Scully MO, Zubairy MS (1997) *Quantum Optics* (Cambridge Univ Press, Cambridge, UK).
- Alicki R (1979) The quantum open system as a model of the heat engine. *J Phys A* 12:L103–L107.
- Boukobza E, Ritsch H (2013) Breaking the Carnot limit without violating the second law: A thermodynamic analysis of off-resonant quantum light generation. *Phys Rev A* 87:063845.
- Kieu TD (2004) The second law, Maxwell's demon, and work derivable from quantum heat engines. *Phys Rev Lett* 93:140403.
- Geva E, Kosloff R (1992) A quantum-mechanical heat engine operating in finite time. A model consisting of spin-1/2 systems as the working fluid. *J Chem Phys* 96:3054–3067.
- Kosloff R (2013) Quantum thermodynamics: A dynamical viewpoint. *Entropy* 15:2100–2128.
- Gemmer J, Michel M, Mahler G (2010) *Quantum Thermodynamics* (Springer, Berlin).
- Scully MO (2010) Quantum photocell: Using quantum coherence to reduce radiative recombination and increase efficiency. *Phys Rev Lett* 104:207701.
- Nalbach P, Thorwart M (2013) Enhanced quantum efficiency of light-harvesting in a biomolecular quantum steam engine. *Proc Natl Acad Sci USA* 110:2693–2694.
- Scully MO, Chapin KR, Dorfman KE, Kim MB, Svidzinsky A (2011) Quantum heat engine power can be increased by noise-induced coherence. *Proc Natl Acad Sci USA* 108:15097–15100.
- Gelbwaser-Klimovsky D, Alicki R, Kurizki G (2013) Work and energy gain of heat-pumped quantized amplifiers. *Europhys Lett* 103:60005.
- Hardal AUC, Müstecaplıoğlu OE (2015) Superradiant quantum heat engine. *Sci Rep* 5:12953.
- Abah O, et al. (2012) Single-ion heat engine at maximum power. *Phys Rev Lett* 109:203006.
- Gelbwaser-Klimovsky D, Alicki R, Kurizki G (2013) Minimal universal quantum heat machine. *Phys Rev E Stat Nonlin Soft Matter Phys* 87:012140.
- Roßnagel J, et al. (2016) A single-atom heat engine. *Science* 352:325–329.
- Gelbwaser-Klimovsky D, Kurizki G (2014) Heat-machine control by quantum-state preparation: From quantum engines to refrigerators. *Phys Rev E* 90:022102.
- Gallego R, Riera A, Eisert J (2014) Thermal machines beyond the weak coupling regime. *New J Phys* 16:125009.
- Lostaglio M, Jennings D, Rudolph T (2015) Description of quantum coherence in thermodynamic processes requires constraints beyond free energy. *Nat Commun* 6:6383.
- Hovhannisyan KV, Perarnau-Llobet M, Huber M, Acín A (2013) Entanglement generation is not necessary for optimal work extraction. *Phys Rev Lett* 111:240401.
- Zhang K, Bariani F, Meystre P (2014) Quantum optomechanical heat engine. *Phys Rev Lett* 112:150602.
- Fialko O, Hallwood DW (2012) Isolated quantum heat engine. *Phys Rev Lett* 108:085303.
- Dorfman KE, Voronine DV, Mukamel S, Scully MO (2013) Photosynthetic reaction center as a quantum heat engine. *Proc Natl Acad Sci USA* 110:2746–2751.
- Steeneken PG, et al. (2011) Piezoresistive heat engine and refrigerator. *Nat Phys* 7:354–359.
- Blickle V, Bechinger C (2012) Realization of a micrometre-sized stochastic heat engine. *Nat Phys* 8:143–146.
- Landsberg PT, Tonge G (1980) Thermodynamic energy conversion efficiencies. *J Appl Phys* 51:R1–R20.
- Scully MO, Zubairy MS, Agarwal GS, Walther H (2003) Extracting work from a single heat bath via vanishing quantum coherence. *Science* 299:862–864.
- Roßnagel J, Abah O, Schmidt-Kaler F, Singer K, Lutz E (2014) Nanoscale heat engine beyond the Carnot limit. *Phys Rev Lett* 112:030602.
- Niedenzu W, Gelbwaser-Klimovsky D, Kofman AG, Kurizki G (2016) On the operation of machines powered by quantum non-thermal baths. *New J Phys* 18:083012.
- Dağ CB, Niedenzu W, Müstecaplıoğlu OE, Kurizki G (2016) Multiatom quantum coherences in micromasers as fuel for thermal and nonthermal machines. *Entropy* 18:244.
- Kolář M, Gelbwaser-Klimovsky D, Alicki R, Kurizki G (2012) Quantum bath refrigeration towards absolute zero: Challenging the unattainability principle. *Phys Rev Lett* 109:090601.
- Correa LA, Palao JP, Alonso D, Adesso G (2014) Quantum-enhanced absorption refrigerators. *Sci Rep* 4:3949.
- Niedenzu W, Mukherjee V, Ghosh A, Kofman AG, Kurizki G (2017) Universal thermodynamic limit of quantum engine efficiency. arXiv 1703.02911.
- Levine IN (2009) *Physical Chemistry* (McGraw-Hill, New York).
- Carmichael H (1999) *Statistical Methods in Quantum Optics* (Springer, Berlin).
- Schleich W (2001) *Quantum Optics in Phase Space* (Wiley-VCH, Berlin).
- Gardiner CW, Zoller P (2000) *Quantum Noise* (Springer, Berlin).
- Louisell WH (1990) *Quantum Statistical Properties of Radiation* (John Wiley & Sons, New York).
- Lutterbach LG, Davidovich L (2000) Production and detection of highly squeezed states in cavity QED. *Phys Rev A* 61:023813.
- Gelbwaser-Klimovsky D, Niedenzu W, Kurizki G (2015) Thermodynamics of quantum systems under dynamical control. *Adv Atom Mol Opt Phys* 64:329–407.
- Pusz W, Woronowicz SL (1978) Passive states and kms states for general quantum systems. *Comm Math Phys* 58:273–290.
- Lenard A (1978) Thermodynamical proof of the Gibbs formula for elementary quantum systems. *J Stat Phys* 19:575–586.
- Brandão F, Horodecki M, Ng N, Oppenheim J, Wehner S (2015) The second laws of quantum thermodynamics. *Proc Natl Acad Sci USA* 112:3275–3279.
- Skrzypczyk P, Short AJ, Popescu S (2014) Work extraction and thermodynamics for individual quantum systems. *Nat Commun* 5:4185.
- Allahverdyan AE, Nieuwenhuizen TM (2000) Extraction of work from a single thermal bath in the quantum regime. *Phys Rev Lett* 85:1799–1802.
- Levy A, Diósi L, Kosloff R (2016) Quantum flywheel. *Phys Rev A* 93:052119.
- Perarnau-Llobet M, et al. (2015) Most energetic passive states. *Phys Rev E* 92:042147.
- Schwabl F (2006) *Statistical Mechanics* (Springer, Berlin).
- Delord T, Nicolas L, Chassagneux Y, Hetet G (2017) Strong coupling between a single NV spin and the torsional mode of diamonds levitating in an ion trap. arXiv:1702.00774.
- Xiang ZL, Ashhab S, You JQ, Nori F (2013) Hybrid quantum circuits: Superconducting circuits interacting with other quantum systems. *Rev Mod Phys* 85:623–653.
- Kurizki G, et al. (2015) Quantum technologies with hybrid systems. *Proc Natl Acad Sci USA* 112:3866–3873.
- Blais A, Huang RS, Wallraff A, Girvin SM, Schoelkopf RJ (2004) Cavity quantum electrodynamics for superconducting electrical circuits: An architecture for quantum computation. *Phys Rev A* 69:062320.
- Gelbwaser-Klimovsky D, et al. (2015) Laser-induced cooling of broadband heat reservoirs. *Phys Rev A* 91:023431.

57. Gelbwaser-Klimovsky D, Kurizki G (2015) Work extraction from heat-powered quantized optomechanical setups. *Sci Rep* 5:7809.
58. Aspelmeier M, Kippenberg TJ, Marquardt F (2014) Cavity optomechanics. *Rev Mod Phys* 86:1391–1452.
59. Lindblad G (1975) Completely positive maps and entropy inequalities. *Commun Math Phys* 40:147–151.
60. Wang MC, Uhlenbeck GE (1945) On the theory of the Brownian motion II. *Rev Mod Phys* 17:323–342.
61. Allahverdyan AE, Balian R, Nieuwenhuizen TM (2004) Maximal work extraction from finite quantum systems. *Europhys Lett* 67:565–571.
62. Paris MGA, Illuminati F, Serafini A, De Siena S (2003) Purity of Gaussian states: Measurement schemes and time evolution in noisy channels. *Phys Rev A* 68: 012314.
63. Olivares S (2012) Quantum optics in phase space: A tutorial on Gaussian states. *Eur Phys J Spec Top* 203:3–24.
64. Dillenschneider R, Lutz E (2009) Energetics of quantum correlations. *Europhys Lett* 88:50003.
65. Li H, et al. (2014) Quantum coherence rather than quantum correlations reflect the effects of a reservoir on a system's work capability. *Phys Rev E* 89:052132.
66. Liao JQ, Dong H, Sun CP (2010) Single-particle machine for quantum thermalization. *Phys Rev A* 81:052121.
67. Qamar S, Zaheer K, Zubairy M (1990) Generation of steady state squeezing in micro-maser. *Opt Commun* 78:341–345.
68. Averbukh I, Sherman B, Kurizki G (1994) Enhanced squeezing by periodic frequency modulation under parametric instability conditions. *Phys Rev A* 50:5301–5308.
69. Niedenzu W, Gelbwaser-Klimovsky D, Kurizki G (2015) Performance limits of multi-level and multipartite quantum heat machines. *Phys Rev E* 92:042123.
70. Jaramillo J, Beau M, del Campo A (2016) Quantum supremacy of many-particle thermal machines. *New J Phys* 18:075019.
71. Gardiner CW (2004) *Handbook of Stochastic Methods* (Springer, Berlin).