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Experimental characterization of a spin quantum heat engine

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Developments in the thermodynamics of small quantum systems envisage non-classical thermal machines. In this scenario, energy fluctuations play a relevant role in the description of irreversibility. We experimentally implement a quantum heat engine based on a spin-1/2 system and nuclear magnetic resonance techniques. Irreversibility at microscope scale is fully characterized by the assessment of energy fluctuations associated with the work and heat flows. We also investigate the efficiency lag related to the entropy production at finite time. The implemented heat engine operates in a regime where both thermal and quantum fluctuations (associated with transitions among the instantaneous energy eigenstates) are relevant to its description. Performing a quantum Otto cycle at maximum power, the proof-of-concept quantum heat engine is able to reach an efficiency for work extraction ($\eta \approx 42\%$) very close to its thermodynamic limit ($\eta = 44\%$).

Quantum thermal machines perform a thermodynamic cycle employing quantum systems as the working medium. This notion was introduced long ago when Scovil and Schulz-Dubois recognized a three-level maser as a kind of heat engine [1], and since then many theoretical proposals for thermodynamical cycles at the quantum scale have been discussed [2–32]. Microscopic quantum heat engines may operate at a scale where both thermal and quantum fluctuations are relevant. The thermodynamic description of such devices operating at finite time should also include the inherent non-deterministic nature of the quantum evolution and non-equilibrium features. In this context, quantities as work, heat, and entropy production are associated with statistical distributions that satisfy fluctuation theorems [33–35] for a thermodynamical cycle [36, 37].

The enthusiastic interest in quantum thermal machines has grown with the possibility to control non-equilibrium dynamics of microscopic systems, achievable in platforms such as: trapped ions [38, 39], quantum dots [40–42], single electron boxes [43], optomechanical oscillators [44–47], etc. Some experimental success related to the implementation of micro-scale heat engines have been reported in a context where quantum coherence effects are not prominent (which can be regarded as a classical context) [48–53]. Recently, a single trapped ion was employed as a working medium to perform a thermodynamic cycle [54]. Despite this latter implementation being based on a single quantum system, the operating temperatures are such that the thermal energy is considerably higher than the energy level separation of the magnetic trap. As a consequence, effects of quantum fluctuations are dwarfed by thermal fluctuations allowing a classical description.

The full characterization of a finite-time operation of a quantum heat engine may also be associated with the assessment of the probability distribution of energy fluctuations, that can take the form of work or heat flow [55]. This assessment embodies significant experimental challenges that remained elusive up to now.

In the present contribution, we used a Nuclear Magnetic Resonance (NMR) setup [56] to implement and characterize a quantum version of the Otto cycle [4]. As a proof-of-concept implementation of a quantum heat engine operating at finite time, we employed a ^{13}C-labeled $CHCl_3$ liquid sample diluted in Acetone-D6 and a 500 MHz Varian NMR spectrometer. The spin 1/2 of the ^{13}C nucleus is the working medium whereas the ^{1}H nuclear spin will be used as a heat bus. High radio-frequency (rf) modes near to Hydrogen Larmor frequency plays the role of the hot environment while low rf modes near to Carbon resonance frequency plays the role of the cold environment. Chlorine isotopes' nuclei provide mild environmental effects. An interferometric method [57–61] is applied to assess energy fluctuations to characterize the work and heat statistics as well as the irreversibility aspects of this spin engine. The operation regime is such that the typical thermal energy scale is of the same order of the typical separation of the quantum energy levels, turning the effects of quantum fluctuations as important as the ones from thermal fluctuations. We have also experimentally endorsed an expression for the efficiency lag related to the entropy production that hinders the implemented engine to attain the Carnot efficiency at finite time. The cycle was established at different finite-time regimes, ranging from a very irreversible to one with almost maximum efficiency, allowing the identification of

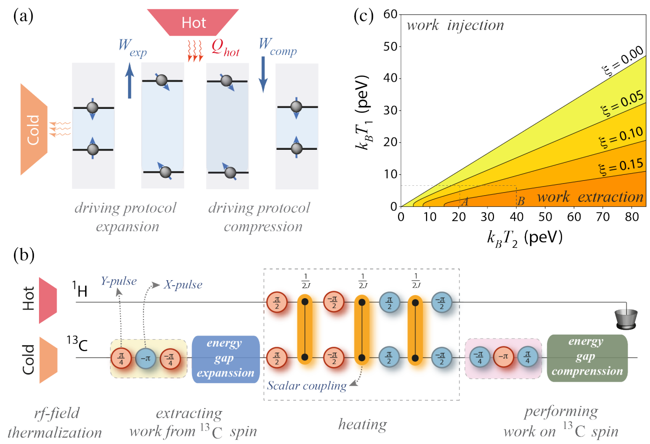

Figure 1. Quantum heat engine schematics. (a) Thermodynamic cycle employing a spin $1/2$ as working medium. (b) Simplified pulse sequence of the experimental protocol. ^{1}H and ^{13}C nuclear spins are initially prepared in thermal states corresponding to hot and cold spin temperatures, respectively. Blue (red) circles represent x (y) rotations by the displayed angle produced by transverse rf pulses. Orange connections stand for free evolutions under the scalar interaction ($\mathcal{H}_J$) during the time displayed above the symbol. The unitary driving for the energy gap expansion (compression) protocol is implemented by a time-modulated rf field resonant with the ^{13}C nuclear spin. The Hydrogen nucleus is used to deliver the heat at the proper part of the cycle, working as a heat bus. (c) Required temperatures for work extraction at finite-time operation mode. The engine extracts work only if the hot (T_2) and cold (T_1) source temperatures correspond to a point below the curve defined by the energy level transition probability ξ.

the maximum power operation.

The quantum version of the Otto cycle [4, 20] consists of a four-stroke protocol as illustrated in Fig. 1(a).

Cooling stroke. Using spatial average techniques employed by rf and gradient fields, the ^{13}C nuclear spin is initially chilled to a pseudo-thermal state, equivalent to $\rho_0^{eq,1} = e^{-\beta_1 \mathcal{H}_1^{\mathrm{C}}} \big/ Z_1$ [62, 63], at a cold inverse spin temperature $\beta_1 = (k_B T_1)^{-1}$, where $Z_1 = \mathrm{tr}\left(e^{-\beta_1 \mathcal{H}_1^{\mathrm{C}}}\right)$ is the partition function, k_B is the Boltzmann constant, T_1 is the absolute spin temperature of the cold reference state, and the Hamiltonian $\mathcal{H}_1^{\mathrm{C}}$ will be defined latter.

Expansion stroke. The working medium Hamiltonian is driven by a time-modulated rf field resonant with the ^{13}C nuclear spin. Initially it can be described by $\mathcal{H}_1^{\mathrm{C}} = -h\nu_1 \sigma_y^{\mathrm{C}}/2$ (with the rf-field intensity adjusted such that $\nu_1 = 2.0$ kHz and $\sigma_{x,y,z}^{\mathrm{C}}$ being the Pauli spin operators for ^{13}C nuclear spin), in a rotating frame at the ^{13}C Larmor frequency ($\approx$125 MHz). From $t = 0$ up to $t = \tau$, the system Hamiltonian is driving according to $\mathcal{H}_{exp}^{\mathrm{C}}(t) = -\frac{1}{2} h\nu(t) \left(\cos\left(\frac{\pi t}{2\tau}\right) \sigma_x^{\mathrm{C}} + \sin\left(\frac{\pi t}{2\tau}\right) \sigma_y^{\mathrm{C}}\right)$, expanding (*exp*) the nuclear spin energy gap linearly as $\nu(t) = \nu_1 \left(1 - \frac{t}{\tau}\right) + \nu_2 \frac{t}{\tau}$ (with $\nu_2 = 3.6$ kHz and $t \in [0, \tau]$).

The energy gap expansion happens in a driving time length, τ, that will be varied in different experiments between 100 μs and 700 μs. The driving time length ($\propto 10^{-4}$s) is much shorter than the typical decoherence time scales, which are on the order of seconds. In this way, we can describe this process by a unitary evolution, $\mathcal{U}_\tau$ [59, 61, 63], that drives the ^{13}C nuclear spin to an out-of-equilibrium state (ρ_τ^{C}), which is, in general, not diagonal in the energy eigenbasis of the final Hamiltonian of the expansion protocol, $\mathcal{H}_2^{\mathrm{C}} = \mathcal{H}_{exp}^{\mathrm{C}}(\tau) = -h\nu_2 \sigma_x^{\mathrm{C}}/2$.

Heating stroke. The working medium (^{13}C nucleus) exchanges heat with the ^{1}H nuclear spin, which was initially prepared in a higher temperature [62, 63] than the ^{13}C nuclear spin, reaching full thermalization at the hot inverse spin temperature $\beta_2 = (k_B T_2)^{-1}$. The full thermalization process is effectively implemented by a sequence of free evolutions under the scalar interaction, $\mathcal{H}_J = \frac{\pi\hbar}{2} J \sigma_z^{\mathrm{H}} \sigma_z^{\mathrm{C}}$ (with $J \approx 215.1$ Hz), between both nuclei and rf pulses to produce suitable rotations as sketched in Fig. 1(b). After thermalization, the state of the ^{13}C nuclei is the hot equilibrium state, equivalent to $\rho_0^{\mathrm{eq},2} = e^{-\beta_2 \mathcal{H}_2^{\mathrm{C}}} \big/ Z_2$.

Compression stroke. Subsequently, an energy gap compression is performed, according to the time-reversed process [64] of the expansion protocol, i.e., the Hamiltonian is driven in a way that $\mathcal{H}_{comp}^{\mathrm{C}}(t) = -\mathcal{H}_{exp}^{\mathrm{C}}(\tau - t)$.

Many cycles of this proof-of-concept experiment can be performed repeating successively the pulse sequence protocol described in Fig. 1(b). It is interesting to note that each experimental run involves spatial averages on a diluted liquid sample containing about 10^{17} molecules, which can be regarded as noninteracting with each other due to the sample dilution. Each experimental result for the quantities of interest represents an average over many copies of a single molecular spin engine.

The finite-time (expansion and compression) driven processes are associated with transitions among the instantaneous eigenstates of the working medium Hamiltonian (see Fig. S3 of [63]) resulting in entropy production [61, 65], which is the main source of irreversibility in the implemented cycle. In this way, quantum coherence also contributes to the irreversibility [66–68].

Considering the aforementioned description of the finite-time thermodynamical cycle, we can write the average values of the extracted work (W_{eng}) from the engine and the absorbed heat (Q_{hot}) from the ^{1}H nuclear spin as

$$\langle W_{eng} \rangle = \frac{h}{2}(\nu_2 - \nu_1)\left[\tanh(\beta_1 h\nu_1) - \tanh(\beta_2 h\nu_2)\right] - h\xi\left[\nu_1 \tanh(\beta_2 h\nu_2) + \nu_2 \tanh(\beta_1 h\nu_1)\right] , \quad (1)$$

$$\langle Q_{hot} \rangle = \frac{h}{2}\nu_2\left[\tanh(\beta_1 h\nu_1) - \tanh(\beta_2 h\nu_2)\right] - \xi h\nu_2 \tanh(\beta_1 h\nu_1) , \quad (2)$$

where $\xi = \left|\left\langle \Psi_{\pm}^{2} \mid \mathcal{U}_{\tau} \mid \Psi_{\mp}^{1}\right\rangle\right|^{2} = \left|\left\langle \Psi_{\pm}^{1} \mid \mathcal{V}_{\tau} \mid \Psi_{\mp}^{2}\right\rangle\right|^{2}$ are the transition probabilities between the instantaneous eigenstates $\left|\Psi_{\pm}^{1}\right\rangle$ ($\left|\Psi_{\pm}^{2}\right\rangle$) of the Hamiltonian $\mathcal{H}_1^{\mathrm{C}}$ ($\mathcal{H}_2^{\mathrm{C}}$) and $\mathcal{V}_{\tau}$ is the unitary evolution describing the compression protocol, satisfying $\mathcal{V}_{\tau} = \mathcal{U}_{\tau}^{\dagger}$. The nuclear spin system operates as a heat engine when $\langle W_{eng}\rangle > 0$, otherwise work is being injected in the device during the cycle. Two conditions must be met to allow work extraction. The first is the requirement that $(\nu_2 - \nu_1)\left[\tanh\left(\beta_1 h\nu_1\right) - \tanh\left(\beta_2 h\nu_2\right)\right] \geq 0$, which is equivalent to the classical-scenario bound, $1 \leq \nu_2/\nu_1 \leq T_2/T_1$. The second condition imposes a limit on the admitted transition probability among the energy levels, which reads

$$\xi \leq \frac{(\nu_2 - \nu_1)\left[\tanh\left(\beta_1 h\nu_1\right) - \tanh\left(\beta_2 h\nu_2\right)\right]}{2\left[\nu_1 \tanh\left(\beta_2 h\nu_2\right) + \nu_2 \tanh\left(\beta_1 h\nu_1\right)\right]}. \tag{3}$$

This condition, illustrated in Fig. 1(c), is related to the rapidity of the energy gap expansion (compression) protocol and to the fact that the driving Hamiltonian does not commute at different times. For a given protocol (that sets the ξ value) the condition (3) only depends on the energy gap compression factor, $r = \nu_2/\nu_1$ ($r \simeq 1.8$ in our experiment). The system operates in the working extraction mode if the point that characterizes the temperature of both heat sources lies below the contour curve in Fig. 1(c) for a given transition probability.

The spin-engine efficiency can be written also in terms of the energy level transition probability as

$$\eta = \frac{\langle W_{eng}\rangle}{\langle Q_{hot}\rangle} = 1 - \frac{\nu_1}{\nu_2}\frac{(1-2\xi\mathcal{F})}{(1-2\xi\mathcal{G})}, \tag{4}$$

where $\mathcal{F} = \tanh\left(\beta_2 h\nu_2\right)\left(\tanh\left(\beta_2 h\nu_2\right) - \tanh\left(\beta_1 h\nu_1\right)\right)^{-1}$ and $\mathcal{G} = \mathcal{F}\tanh\left(\beta_1 h\nu_1\right)/\tanh\left(\beta_2 h\nu_2\right)$. The Otto limit ($\eta_{\mathrm{Otto}}$) is recovered in an adiabatic (transitionless, i.e. $\xi = 0$) driving. On the other hand, in the finite-time regime the efficiency (4) decreases as ξ increases. Alternatively, we can derive an expression for the engine efficiency in terms of efficiency lags (associated with entropy production [29–31, 61]) as $\eta = \eta_{\mathrm{Carnot}} - \mathcal{L}$, and the lag is given by [63]

$$\mathcal{L} = \frac{\mathcal{S}\left(\mathcal{U}_{\tau}\rho_0^{eq,1}\mathcal{U}_{\tau}^{\dagger}\middle\|\,\rho_0^{eq,2}\right) + \mathcal{S}\left(\mathcal{V}_{\tau}\rho_0^{eq,2}\mathcal{V}_{\tau}^{\dagger}\middle\|\,\rho_0^{eq,1}\right)}{\beta_1\langle Q_{hot}\rangle}, \tag{5}$$

where $\mathcal{S}\left(\rho_a\|\,\rho_b\right) = \mathrm{tr}\left[\rho_a\left(\ln\rho_a - \ln\rho_b\right)\right]$ is the relative entropy and $\eta_{\mathrm{Carnot}} = 1 - T_1/T_2$ the standard Carnot efficiency.

Work extracted from (performed on) the ^{13}C nuclear spin during the energy gap expansion (compression) driving protocol is actually a stochastic variable, described by a probability distribution [36, 37], $P_{exp}(W)$ ($P_{comp}(W)$). The full thermalization with the hot source allows us to write the work performed in each Hamiltonian driving stroke of the cycle as independent variables. So, the net extracted work from the engine is a convolution of the two marginal work probability distributions, which can be assessed by the interferometric approach [59, 61]. In the present experiment, the characteristic function of the work probability distribution is measured. In the energy gap expansion stroke, it is given by

$$\begin{aligned}\chi_{exp}(u) &= \mathrm{tr}\left[\mathcal{U}_{\tau}e^{-iu\mathcal{H}^{\mathrm{C}}_{\exp,0}}\rho_0^{\mathrm{eq},1}\left(e^{-iu\mathcal{H}^{\mathrm{C}}_{\exp,\tau}}\mathcal{U}_{\tau}\right)^{\dagger}\right] \\ &= \sum_{n,m=0}^{1} p_n^0 p_{m|n}^{\tau} e^{iu\left(\epsilon_m^{\tau} - \epsilon_n^0\right)}\,,\end{aligned} \tag{6}$$

where p_n^0 is the occupation probability of the n-th energy level in the cold initial thermal state ($\rho_0^{\mathrm{eq},1}$), $p_{m|n}^{\tau} = \xi + (1-2\xi)\,\delta_{m,n}$ is the transition probability between the Hamiltonian eigenstates induced by the time-dependent quantum dynamics, ϵ_m^{τ} and ϵ_n^0 are eigenenergies of the Hamiltonians $\mathcal{H}_1^{\mathrm{C}}$ and $\mathcal{H}_2^{\mathrm{C}}$, respectively. Analogous expressions hold for the compression stroke ($\chi_{comp}(u)$) [63]. The characteristic function for the engine net work is the product of characteristic functions for both Hamiltonian driving protocols, i.e. $\chi_{eng}(u) = \chi_{comp}(u)\chi_{exp}(u)$. Thus, the inverse Fourier transform of the measured $\chi_{eng}(u)$ provides the work probability distribution for the quantum engine as $P_{eng}(W) = \int du\chi_{eng}(u)e^{iuW}$ and the mean value of the extracted work can be obtained from the statistics as $\langle W_{eng}\rangle = \int dW P_{eng}(W)W$.

We characterized the work distribution in different operation modes of the spin engine, varying the driving time length (τ) and the hot source temperature, with representative results displayed in Fig. 2. The initial spin temperatures of the ^{1}H and ^{13}C nuclei were verified by quantum

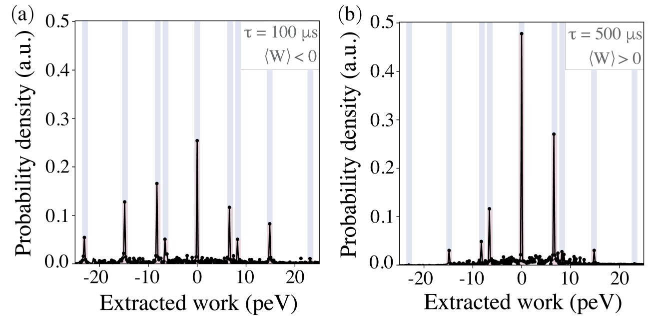

Figure 2. Extracted work probability distribution of the quantum engine with Hamiltonian driving time lengths: (a) $\tau = 100\,\mu$s and (b) $\tau = 500\,\mu$s. Cold and hot source temperatures are set at $k_B T_1 = (6.6 \pm 0.1)$ peV and $k_B T_2^B = (40.5 \pm 3.7)$ peV, respectively. The experimental data (points) is well fitted by a sum of nine Lorentzian peaks (the full line) centered approximately at 0, $\pm h\left(\nu_2 - \nu_1\right)$, $\pm\nu_1$, $\pm\nu_2$, and $\pm h\left(\nu_2 + \nu_1\right)$ (dashed columns), in agreement with the theoretical expectation (see supplemental Fig. S3 in [63]). The error bars are smaller than the symbols size and are not shown.

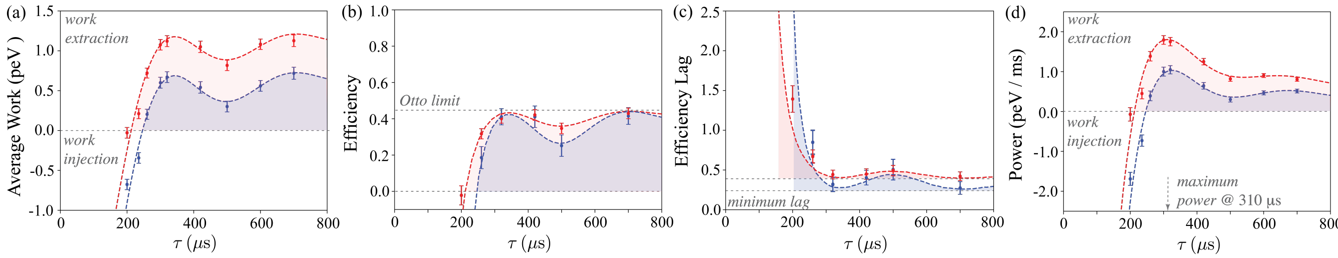

Figure 3. Spin quantum engine figures of merit: (a) average extracted work, (b) efficiency, (c) efficiency lag due to entropy production cf. Eq. (5) (the minimum lag is $\eta_{\text{Carnot}} - \eta_{\text{Otto}}$), and (d) extracted power, as a function of the driving protocol time length (τ). Points represent experimental data. The dashed lines are based on theoretical predictions and numerical simulations. In all experiments, the spin temperature of the cold source is set at $k_B T_1 = (6.6 \pm 0.1)$ peV. Data in blue and red correspond to implementations with the hot source spin temperatures set at $k_B T_2^A = (21.5 \pm 0.4)$ peV and $k_B T_2^B = (40.5 \pm 3.7)$ peV, respectively.

state tomography (QST) [56], which confirmed the Gibbs state preparation. The spin temperature of the ^{13}C cold initial state is equivalent to $k_B T_1 = (6.6 \pm 0.1)$ peV, while the ^{1}H was prepared in two hot states (A and B) corresponding to $k_B T_2^A = (21.5 \pm 0.4)$ peV and $k_B T_2^B = (40.5 \pm 3.7)$ peV.

There are nine observed peaks in Fig. 2(a), corresponding to the fastest implemented engine driving. A fit of these experimental data allows us to determine the transition probability ξ that vary from $\xi = 0.02 \pm 0.02$ (for $\tau = 700$ μs) to $\xi = 0.38 \pm 0.04$ (for $\tau = 100$ μs). We observe that when the Hamiltonian driving is slower, as in Fig. 2(b), some of the work distribution peaks get decreased to the point of being barely noticeable amid the noise (associated with the Fourier analysis), since the dynamics is getting closer to the adiabatic one. We also characterize the Hamiltonian driving protocol by means of quantum process tomography [69, 70] to certify that it implements an almost unitary process [63].

The absorbed heat from the hot source (^{1}H nuclear spin) is also a stochastic variable and its probability distribution, $\mathcal{P}(Q)$, could be assessed by a two-time energy measurement scheme [71]. However, in a full thermalization process, the measurement of energy at the end of the process is uncorrelated with the measurement at the start. Then, two QSTs are enough to provide a direct evaluation of the heat probability distribution in the present implementation [63]. One of them is done at the end of the energy gap expansion stroke (where the state is typically out-of-equilibrium), while the other is done at the start of the energy gap compression stroke (and thus should result in the hot thermal state). So the mean heat from the hot source can be expressed as $\langle Q_{hot} \rangle = \int dQ \mathcal{P}(Q) Q$.

With the aforementioned data, we have fully characterized the quantum heat engine. Its performance can be rated according to the average work extracted per cycle, efficiency, efficiency lag, and the average delivered power. These figures of merit are shown in Fig. 3(a)-3(d). The work extraction regime requires a lower bound on the driving time length, as can be seen in Fig. 3(a) and also was anticipated by condition (3). If the engine is operated at a too-fast driving time length τ (smaller than $\approx 200\,\mu$s in this case), the entropy production is so large that it is not possible to extract work. This entropy production decreases with a slower operation rate, although not monotonically. The latter fact is a consequence of the specific form of the Hamiltonian time modulation employed in our implementation and does not generalize to other drivings.

Figure 3(b) illustrates that slower operation leads to better efficiency. Nonetheless, the quantum engine irreversibility can also be characterized by the efficiency lag (5) measured by QST at different strokes. We observe a complete agreement between the lag displayed in Fig. 3(c) and the efficiency measured as the mean work and heat ratio [Fig. 3(b)]. For the implemented quantum cycle, the main source of irreversibility is the divergence (accounted by the relative entropy) of the state achieved after the Hamiltonian driving protocols (expansion and compression) and the reference (hot and cold) thermal states.

We are often interested in power, and a too-slow engine operation, as an adiabatic dynamics, cannot deliver a fairly good amount of power. Extracted power is maximized when the energy gap expansion (compression) protocol takes about $310\,\mu$s as can be noted in Fig. 3(d). Quicker protocols are worse due to considerable entropy production associated with energy level transitions during the dynamics [Fig. 3(c)], while slower driven protocols are also worse since they take more time to deliver a similar amount of work [Fig. 3(a)]. The effective full thermalization with the hot source (^{1}H nucleus) employed in our experiment [central part of the pulse sequence in Fig. 1(b)] lasts for about 7 ms and it takes the same time length in all operation modes of the spin engine. In this fashion, we have opted to describe all results in terms of the expansion and compression Hamiltonian driving time length τ, which is the finite-time feature in the present spin engine implementation.

We performed an experimental proof-of-concept of a quantum heat engine based on a nuclear spin where the typical energy gaps, about 8.27 peV, are of the order of heat source energy, $k_B\,(T_2 - T_1)$ ($\approx$ 15 peV). The extracted work per cycle may be on the same order of magnitude (few peV) depending on the driving protocol. At maximum power ($\tau \approx 310$ μs), the engine efficiency, $\eta = 42 \pm 6\%$, is very close to the Otto limit, $\eta_{Otto} = 44\%$, for the compression factor employed in the present implementation. The power delivered by the quantum engine, in the finite-time operation mode, is ultimately limited by quantum fluctuations (transitions among the instantaneous energy eigenstates), which are also related to entropy production [61, 65] leading to a "quantum friction" [29, 30]. Assessing the statistics of energy fluctuations in the implemented engine, we fully characterize its irreversibility and efficiency lag. The investigation of this data can also allow the quantum engine optimization by choosing optimal driving protocols.

The methods employed here to assess energy fluctuations and to characterize irreversibility in the quantum engine are versatile and can be applied to other experimental settings. The developed spin engine architecture is a comprehensive platform for future investigations of thermodynamical cycles at micro-scale, which would involve, for instance, non-equilibrium, non-classical, and correlated heat sources, allowing the detailed study of a plethora of effects in quantum thermodynamics [23, 24].

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