Single-atom heat machines enabled by energy quantization:supplementary information

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I. OTTO CYCLE

The Otto cycle is composed of four strokes that connect different states of the system (A, B, C, D), as follows:
1) At A, the particle of mass m is in the confining potential V_h. The Hamiltonian is $H_h = \frac{p^2}{2m} + V_h(x)$, where p is the momentum operator. The system is at thermal equilibrium with the hot bath at temperature T_h, hence the population of the n^{th} level is $P_{n,A} = Z_h^{-1} e^{-\frac{E_{n,h}}{k_B T_h}}$, where $E_{n,h}$ is the n^{th}-level eigenenergy of H_h and $Z_h = \sum_n e^{-\frac{E_{n,h}}{k_B T_h}}$. The potential can be parametrized by a generalized volume $\mathcal{V}_h$ [1]. The system is decoupled from the hot bath and the trap is adiabatically deformed until the potential $V_c(x)$ with generalized volume $\mathcal{V}_c$ is obtained at B. The Hamiltonian at B is $H_c = \frac{p^2}{2m} + V_c(x)$. Adiabaticity ensures that the level populations do not change, $P_{n,B} = P_{n,A}$. The change in energy of the system can be attributed purely to work, W_{AB}.
2) Next, the system is coupled to a cold thermal bath at temperature T_c and it reaches thermal equilibrium at C (see SI-VII). Thus, $P_{n,C} = Z_c^{-1} e^{-\frac{E_{n,c}}{k_B T_c}}$, where $E_{n,c}$ is the n^{th}-level eigenenergy of H_c and $Z_c = \sum_n e^{-\frac{E_{n,c}}{k_B T_c}}$. The trapping potential and its volume do not change; the change in energy of the system can be attributed to heat exchange with the cold bath Q_c.
3) Next, the system is decoupled from the cold bath and the potential is adiabatically transformed, returning to V_h with volume $\mathcal{V}_h$ at D. The level populations do not change, $P_{n,D} = P_{n,C}$, and all energy exchanged is work, W_{CD}.
4) The system is coupled to the hot bath, ending at thermal equilibrium with it at A, and closing the thermodynamic cycle. The potential is kept constant and the exchanged energy is heat with the hot bath, Q_h.

The heat exchanged with the baths is given by the energy difference between the initial and final states of the isochoric strokes (see SI-VII):

$$Q_h = \langle H_h \rangle_A - \langle H_h \rangle_D = \sum_n E_{n,h} \left(\frac{e^{-\frac{E_{n,h}}{k_B T_h}}}{Z_h} - \frac{e^{-\frac{E_{n,c}}{k_B T_c}}}{Z_c} \right),$$
$$Q_c = \langle H_c \rangle_C - \langle H_c \rangle_B = \sum_n E_{n,c} \left(\frac{e^{-\frac{E_{n,c}}{k_B T_c}}}{Z_c} - \frac{e^{-\frac{E_{n,h}}{k_B T_h}}}{Z_h} \right). \tag{S1}$$

After completing a cycle, the energy of the system returns to its initial value. Therefore, by energy conservation, the net work is

$$W = -Q_h - Q_c = \sum_n (E_{n,c} - E_{n,h}) \left(\frac{e^{-\frac{E_{n,h}}{k_B T_h}}}{Z_h} - \frac{e^{-\frac{E_{n,c}}{k_B T_c}}}{Z_c} \right). \tag{S2}$$

Positive work or heat implies an energy flow into the system and a negative value signifies an energy flow out of the system. If the potential deformation does not change the expected value of the energies, no work is extracted.

For an homogenous scaling of the energies, $E_{n,h} = qE_{n,c}$, the expression for the work can be rewritten as

$$W = \sum_n (1-q) \frac{E_{n,h}}{q} \left(\frac{e^{-\frac{E_{n,h}}{k_B T_h}}}{Z_h} - \frac{e^{-\frac{E_{n,h}}{k_B q T_c}}}{Z_c} \right) = \frac{(1-q)}{q} \times$$
$$(f_h - f_{qT_c}) = \frac{(1-q)}{q} \int_{qT_c}^{T_h} \frac{df_T}{dT} dT = \frac{(1-q)}{q} \int_{qT_c}^{T_h} C_v dT, \tag{S3}$$

where $Z_T = \sum_m e^{-\frac{E_{m,h}}{k_B T}}$, $f_T \equiv \sum_n E_{n,h} \frac{e^{-\frac{E_{n,h}}{k_B T}}}{Z_T}$, $C_v \equiv \frac{\partial \langle H_h \rangle_T}{\partial T}$ is the heat capacity, and $\langle\rangle_T$ is the expected value in the thermal Boltzmann distribution at temperature T.

II. WORK AND EFFICIENCY FOR A TWO LEVEL SYSTEM

If only the first two levels are populated Eq. (S2) can be simplified to

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$$W = (E_{g,c} - E_{g,h})\times \left(\frac{e^{-\frac{E_{g,h}}{k_BT_h}}}{e^{-\frac{E_{g,h}}{k_BT_h}}+e^{-\frac{E_{e,h}}{k_BT_h}}} - \frac{e^{-\frac{E_{g,c}}{k_BT_c}}}{e^{-\frac{E_{g,c}}{k_BT_c}}+e^{-\frac{E_{e,c}}{k_BT_c}}}\right) + (E_{e,c} - E_{e,h})\left(\frac{e^{-\frac{E_{e,h}}{k_BT_h}}}{e^{-\frac{E_{g,h}}{k_BT_h}}+e^{-\frac{E_{e,h}}{k_BT_h}}} - \frac{e^{-\frac{E_{e,c}}{k_BT_c}}}{e^{-\frac{E_{g,c}}{k_BT_c}}+e^{-\frac{E_{e,c}}{k_BT_c}}}\right)$$
$$= \frac{(\Delta_h - \Delta_c)(e^{-(\frac{E_{g,h}}{k_BT_h}+\frac{E_{e,c}}{k_BT_c})} - e^{-(\frac{E_{g,c}}{k_BT_c}+\frac{E_{e,h}}{k_BT_h})})}{(e^{-\frac{E_{g,h}}{k_BT_h}}+e^{-\frac{E_{e,h}}{k_BT_h}})(e^{-\frac{E_{g,c}}{k_BT_c}}+e^{-\frac{E_{e,c}}{k_BT_c}})},$$

where $\Delta_i = E_{e,i} - E_{g,i}$. Therefore, the condition for work extraction, $W < 0$, is

$$\frac{T_h}{T_c} > \frac{\Delta_h}{\Delta_c} > 1.$$

In a similar way, the heat exchanged with the hot bath is

$$Q_h = \Delta_h \frac{e^{-(\frac{E_{g,h}}{k_BT_h}+\frac{E_{e,c}}{k_BT_c})} - e^{-(\frac{E_{e,c}}{k_BT_c}+\frac{E_{e,h}}{k_BT_h})}}{(e^{-\frac{E_{g,h}}{k_BT_h}}+e^{-\frac{E_{e,h}}{k_BT_h}})(e^{-\frac{E_{g,c}}{k_BT_c}}+e^{-\frac{E_{e,c}}{k_BT_c}})},$$

and the efficiency is

$$\eta^{en} = -\frac{W}{Q_h} = 1 - \frac{\Delta_c}{\Delta_h}.$$

For the cycle shown in figure 1B in the main text, $\Delta_h = \frac{3\hbar^2\pi^2}{2mL_h^2}$ and $\Delta_c = \Delta_{c,box} + \Delta E_{c,\delta}$, where $\Delta_{c,box} = \frac{3\hbar^2\pi^2}{2mL_c^2}$. Therefore,

$$\frac{\Delta_c}{\Delta_h} = \frac{\Delta_{c,box}}{\Delta_h}\left(\frac{\Delta_c}{\Delta_{c,box}}\right) = \frac{1}{r^2}\left(\frac{\Delta_c}{\Delta_c - \Delta E_{c,\delta}}\right) = \frac{1}{r^2}\left(\frac{1}{1-\frac{\Delta E_{c,\delta}}{\Delta_c}}\right), \quad \text{(S4)}$$

where we have used the fact that $r^2 = \frac{\Delta_h}{\Delta_{c,box}} = \frac{L_c^2}{L_h^2}$. From here the right side of Eq. 3 in the main text is derived.

III. THERMODYNAMIC CALCULATIONS FOR THE CLASSICAL HEAT MACHINE

There are multiple alternative methods to calculate the Q_h, Q_c and W for the classical heat machine studied in the main text. All of them give the same results:

1. Doing the quantum calculation using Eqs. (S1) and (S2), and effectively reducing $\hbar$ until the result converges. In the studied cases the convergences was obtained for $\hbar_{eff}/\hbar = 10^{-2}$;
2. Considering the same scaling for the potential and temperatures, $V_i \to \xi^2 V_i$ and $T_{c(h)} \to \xi^2 T_{c(h)}$ and taking the limit $\xi \to \infty$;
3. In the case of the infinite square well, the $\delta-$barrier does not change the energy at the classical limit, the standard Otto cycle calculation can be used, neglecting the $\delta-$barrier.

IV. EXPERIMENTAL SIMULATION OF THE CLASSICAL LIMIT

In this section we show that the classical limit of the extracted work, (S2), is equivalent to the work obtained after scaling the potential and the temperature. A similar proof can be used for the heats.

In order to find the classical limit, in the Schrodinger equation $\hbar$ is replaced by $\hbar_{eff} = \frac{\hbar}{\xi}$, where ξ is scaling parameter in the range between 1 and ∞. The Schrodinger equation is

$$\left[-\left(\frac{\hbar^2}{\xi^2}\right)\frac{1}{2m}\frac{\partial^2}{\partial^2 x} + V(x)\right]\psi_n(x) = E_n\left(\hbar_{eff} = \frac{\hbar}{\xi}, V(x)\right)\psi_n(x), \quad \text{(S5)}$$

where the eigenenergies depend on $\hbar_{eff}$ and on $V(x)$. By multiplying both side by ξ^2,

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 x} + \xi^2 V(x)\right]\psi_n(x) = \xi^2 E_n\left(\hbar_{eff} = \frac{\hbar}{\xi}, V(x)\right)\psi_n(x). \quad \text{(S6)}$$

Therefore, we conclude that,

$$E_n\left(\hbar_{eff} = \hbar, \xi^2 V(x)\right) = \xi^2 E_n\left(\hbar_{eff} = \frac{\hbar}{\xi}, V(x)\right). \quad \text{(S7)}$$

The work is a linear combination of terms of the form,

$$\sum_n E_n\left(\hbar_{eff} = \frac{\hbar}{\xi}, V_a(x)\right)\frac{e^{-\frac{E_n\left(\hbar_{eff}=\frac{\hbar}{\xi}, V_b(x)\right)}{k_BT}}}{Z_{T,\hbar_{eff}=\frac{\hbar}{\xi},V_b(x)}}, \quad \text{(S8)}$$

where $V_a(x)$ and $V_b(x)$ may be the same or different potentials and $Z_{T,\hbar_{eff}=\frac{\hbar}{\xi},V_b(x)} = \sum_n e^{-\frac{E_n(\hbar_{eff}=\frac{\hbar}{\xi},V_b(x))}{k_BT}}$. Using Eq. (S7) we get

$$\sum_n \frac{E_n\left(\hbar_{eff} = \hbar, \xi^2 V_a(x)\right)}{\xi^2}\frac{e^{-\frac{E_n\left(\hbar_{eff}=\hbar,\xi^2 V_b(x)\right)}{k_B\xi^2 T}}}{Z_{\xi^2 T,\hbar_{eff}=\hbar,\xi^2 V_b(x)}}.$$

From this we conclude that

$$W(\hbar_{eff}=\frac{\hbar}{\xi},V_a(x),V_b(x),T_h,T_c)=$$
$$\frac{W(\hbar_{eff}=\hbar,\xi^2V_a(x),\xi^2V_b(x),\xi^2T_h,\xi^2T_c)}{\xi^2}. \tag{S9}$$

The classical limit is obtained for large ξ when $W(\hbar_{eff}=\frac{\hbar}{\xi},V_a(x),V_b(x),T_h,T_c)$ becomes a constant as function of $\hbar_{eff}=\frac{\hbar}{\xi}$. Thus, by scaling the potential and the temperature by a large factor, $\xi\to\infty$, it is possible to experimentally simulate the classical limit, $\hbar\to 0$.

The scaling of a potential and the temperature has been achieved in ion traps setups [2–6]. Therefore, we consider them as the ideal platform to test the classical and quantum limit of the same heat machine.

V. CARNOT LIMIT

In this section we prove that the efficiency of the Otto quantum heat machine is bounded by the Carnot limit, $\eta^{en}_{car}=1-\frac{T_c}{T_h}$. We focus on the heat engine efficiency but the bounds for the performance of a refrigerator can be derived in the same way. The efficiency of a heat engine is

$$\eta^{en}=\frac{-W}{Q_h}.$$

Work extraction requires $W<0$ and $Q_h>0$. The expression for the heat and the work are given by Eqs. S1 and S2 on the SI-I. As a first step, assume that the work and heat are produced by a single level,

$$W_n=(E_{c,n}-E_{h,n})\left(\frac{e^{-\frac{E_{h,n}}{k_BT_h}}}{Z_h}-\frac{e^{-\frac{E_{c,n}}{k_BT_c}}}{Z_c}\right);$$
$$Q_{h,n}=E_{h,n}\left(\frac{e^{-\frac{E_{h,n}}{k_BT_h}}}{Z_h}-\frac{e^{-\frac{E_{c,n}}{k_BT_c}}}{Z_c}\right). \tag{S10}$$

Work extraction requires $\frac{E_{h,n}}{T_h}<\frac{E_{c,n}}{T_c}$, otherwise, $W>0$. Therefore, the single level efficiency is bounded,

$$\eta^{en}_n=1-\frac{E_{c,n}}{E_{h,n}}\le 1-\frac{T_c}{T_h}. \tag{S11}$$

Next we consider two levels, n and m. We prove that the efficiency in the case of two levels can not be greater that the efficiency of a single level and therefore the two level case is also bounded by the Carnot limit. Assume that the efficiency of the two levels is greater than the single level efficiency,

$$\frac{-W_n-W_m}{Q_{h,n}+Q_{h,m}}>\frac{-W_n}{Q_{h,n}}. \tag{S12}$$

Work extraction requires $Q_{h,n}+Q_{h,m}>0$, thus $Q_{h,n}$ or $Q_{h,m}$ should be positive. Without loss of generality we assume $Q_{h,n}>0$ and $\eta^{en}_n\ge\eta^{en}_m$. Hence, Eq. (S12) can be rewritten as

$$\frac{-W_m}{Q_{h,m}}>\frac{-W_n}{Q_{h,n}}. \tag{S13}$$

Equation (S13) contradicts the assumption $\eta^{en}_n\ge\eta^{en}_m$. Thus, the inequality on Eq. (S12) does not hold. This can be generalized for a multilevel system. Therefore, the efficiency of a multilevel system can not be greater than the highest single-level efficiency. The latter, and therefore the whole multilevel efficiency, is bounded by the Carnot limit, (see Eq. (S11)).

VI. FINITE TIME OTTO CYCLE

We consider a simple model of a finite time Otto cycle where the system does not fully equilibrate with the thermal baths during the isochoric strokes. Instead, we assume that the isochoric strokes are interrupted before equilibration and the system ends in a mixture of the initial state and the thermal state, i.e.,

$$\rho_{no-th}=p\rho_0+(1-p)\rho_{th},$$

where ρ_o is the initial state of the system at the beginning of the isochoric stroke and ρ_{th} is the equilibrium state it would have reached after infinite time. p is a constant that represents the degree of thermalization and goes from 0 for a fully equilibrium state, to 1 for a state that did not thermalize at all. For simplicity we assume that the degree of thermalization is symmetric, i.e., it is the same for the two isochoric strokes. The heat transfer from the hot bath is

$$Q^{inc}_h=\langle H_h\rangle_{\rho_{no-th}}-\langle H_h\rangle_{\rho_0}=$$
$$Tr[H_h(p\rho_0+(1-p)\rho_{th})]-Tr[H_h\rho_0]=$$
$$Tr[H_h(p\rho_0+(1-p)\rho_{th})]-Tr[H_h(p+1-p)\rho_0]=$$
$$(1-p)\left(Tr[H_h\rho_{th}]-Tr[H_h\rho_0]\right)=(1-p)Q_h, \tag{S14}$$

where Q_h is the heat exchanged if the system fully thermalizes (see Eq. S1). A similar expression is found for Q^{inc}_c. Therefore, the work extracted during this cycle is

$$W^{inc}=-Q^{inc}_h-Q^{inc}_c=-(1-p)W,$$

but the efficiency, being the ration between W^{inc} and Q^{inc}_{hc}, remains the same, and the operation mode of the heat machine does not change. Therefore, if the degree of thermalization is symmetric, the effects shown in the main text do not change. More complex finite time cycles could be considered, but they are out of scope of this paper and are left for future works.

VII. IRREVERSIBILITY OF THE ISOCHORIC PROCESS

During the isochoric process the working substance is coupled to a thermal bath which not necessary is close to the working substance temperature which makes the process irreversible. In addition, in the quantum system, the state after the adiabatic step prior to the isochoric process is in general not a thermal state. However, the fact that the isochoric process is irreversible does not change the efficiency of the Otto engine. The efficiency is defined in terms of the work done by the engine, and the heat received by the engine from the hot reservoir [7]. No work is done during the isochoric process, and therefore the work done is not affected by irreversibility. Furthermore, the heat exchanged during each isochoric process is given by the internal energy difference of the working substance between the beginning and the end of the isochoric process, and is path independent. Therefore the heat exchanged by the engine and the reservoir is also not affected by irreversibility. Consequently the efficiency of the Otto engine is not affected by the irreversibility of the isochoric process. This is also the conclusion reached after Eq. 17 of Ref. [8]. Note that this argument does not hold for other processes where work is exchanged while the system is coupled to a bath.

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