

Quantum thermodynamic cycles and quantum heat engines. II.

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We study the quantum-mechanical generalization of force or pressure, and then we extend the classical thermodynamic isobaric process to quantum-mechanical systems. Based on these efforts, we are able to study the quantum version of thermodynamic cycles that consist of quantum isobaric processes, such as the quantum Brayton cycle and quantum Diesel cycle. We also consider the implementation of the quantum Brayton cycle and quantum Diesel cycle with some model systems, such as single particle in a one-dimensional box and single-mode radiation field in a cavity. These studies lay the microscopic (quantum-mechanical) foundation for Szilard-Zurek single-molecule engine.

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I. INTRODUCTION

Quantum thermodynamics is the study of heat and work dynamics in quantum-mechanical systems [1]. In the extreme limit of small systems with only a few degrees of freedom, both the finite-size effect and quantum effects influence the thermodynamic properties of the system dramatically [2–4]. The traditional thermodynamic theory based on classical systems of macroscopic size does not apply anymore, and the quantum-mechanical generalization of thermodynamics becomes necessary. The interplay between thermodynamics and quantum physics has been an interesting research topic since the 1950s [5]. In recent years, with the developments of nanotechnology and quantum information processing, the study of the interface between quantum physics and thermodynamics began to attract more and more attention [6]. Studies of quantum thermodynamics not only promise important potential applications in nanotechnology and quantum information processing, but also bring new insights to some fundamental problems of thermodynamics, such as Maxwell’s demon and the universality of the second law [7]. Among all the studies about quantum thermodynamics, a central concern is to make a quantum-mechanical extension of classical thermodynamic processes and cycles [8].

It is well known that in classical thermodynamics there are four basic thermodynamic processes: adiabatic process, isothermal process, isochoric process, and isobaric process [9]. These four processes correspond to constant entropy, constant temperature, constant volume, and constant pressure, respectively. From these four basic thermodynamic processes, we can construct all kinds of thermodynamic cycles, such as the Carnot cycle, Otto cycle, Brayton cycle, etc. [10]. Among all the four kinds of basic thermodynamic processes, the adiabatic process has been extended to the quantum domain and has been extensively studied ever since the birth of quantum mechanics. Nevertheless, no attention was paid to the quantum-mechanical generalization of the remaining three basic thermodynamic processes until most recently. In a recent paper [8], along with our collaborators, we systematically study the quantum-mechanical generalization of the isothermal and isochoric processes. Based on these studies, the properties of the quantum Carnot cycle and quantum Otto cycle are clarified. Meanwhile, in recent years, numerous

studies on other quantum thermodynamic cycles have also been reported [11]. However, as to our best knowledge, the quantum-mechanical generalization of the isobaric process (constant pressure) has not been studied systematically so far. Possibly the lack of the consideration of the quantum isobaric process is due to the fact that “pressure” (force) [12] is not a well-defined observable in a quantum-mechanical system. Because of the lack of a well-defined “pressure” (force) and thus the quantum isobaric process, the properties of quantum thermodynamic cycles that consist of the quantum isobaric process, such as the quantum Brayton cycle and quantum Diesel cycle [9,10], cannot be clarified. We notice that some discussions about quantum Brayton cycle have been reported [13]. Nevertheless, their definitions of the quantum isobaric process and quantum Brayton cycle are ambiguous, and even in contradiction sometimes. As a result, in their studies they cannot bridge the quantum and classical thermodynamic cycles.

In this paper, along with our previous effort [8], we will focus on the study of the quantum isobaric process [10] and its related quantum thermodynamic cycles. We begin with the definition of “pressure” for an arbitrary quantum system, and then generalize the isobaric process to quantum-mechanical systems. Based on this and our previous [8] generalizations of thermodynamic processes, we are able to study an arbitrary quantum thermodynamic cycle constructed by any of these four quantum thermodynamic processes. As an example, we will discuss the quantum Brayton cycle and the quantum Diesel cycle and compare their properties with their classical counterparts. Comparisons between these quantum thermodynamic cycles and their classical counterparts enable us to extend our understanding about the thermodynamics at the interface of classical and quantum physics. This paper is organized as follows: In Sec. II, we define microscopically “pressure” for an arbitrary quantum-mechanical system and study the quantum-mechanical generalization of the isobaric process; in Sec. III, we study the quantum Brayton cycle and study how the efficiency of the Brayton cycle bridges quantum and classical thermodynamic cycles; in Sec. IV we study the quantum Diesel cycle in comparison with its classical counterpart; Sec. V contains the remarks and conclusion.

II. QUANTUM ISOBARIC PROCESS

A. Pressure in quantum-mechanical system

In order to study the quantum isobaric process, we must first study pressure in an arbitrary quantum-mechanical system. Let us recall that in some previous work [8,14], heat and work have been extended to quantum-mechanical systems and expressed as functions of the eigenenergies E_n and probability distributions P_n . The first law of thermodynamics has also been generalized to quantum-mechanical systems as follows:

$$dQ = \sum_n E_n dP_n,$$

$$dW = \sum_n P_n dE_n,$$

$$dU = dQ + dW = \sum_n (E_n dP_n + P_n dE_n), \quad (1)$$

where E_n is the n th eigenenergy of the quantum-mechanical system with the Hamiltonian $H = \sum_n E_n |n\rangle\langle n|$ under consideration; P_n is the occupation probability in the n th eigenstate; $|n\rangle$ is the n th eigenstate of the Hamiltonian. The density matrix of the system can be written as $\rho = \sum_n P_n |n\rangle\langle n|$. dQ and dW depict the heat exchange and work done, respectively, during a thermodynamic process. From classical thermodynamics we know that the first law can be expressed as $dU = dQ + dW = TdS + \sum_n Y_n dy_n$. Here, T and S refer to temperature and thermodynamic entropy, Y_n is the generalized force, and y_n is the generalized coordinate corresponding to Y_n (dy_n is the generalized displacement) [15]. Inversely, the generalized force conjugate to the generalized coordinate y_n can be expressed as [16]

$$Y_n = - \frac{dW}{dy_n}. \quad (2)$$

For example, when the generalized coordinate is chosen to be the volume V , we have its corresponding generalized force-pressure $P = -dW/dV$. Motivated by the definition of the generalized force for a classical system, we define analogously the force [for a one-dimensional (1D) system, force is the same as pressure] for a quantum-mechanical system

$$F = - \frac{dW}{dL} = - \sum_n P_n \frac{dE_n}{dL}, \quad (3)$$

where L is the generalized coordinate corresponding to the force F . In obtaining Eq. (3), we have used the expression of work for a quantum system $dW = \sum_n P_n dE_n$. For a single particle in a 1D box (1DB) [17] (see Fig. 1), the generalized coordinate is the width of the potential, and the eigenenergies for such a system depend on the generalized coordinate $E_n(L) = (\pi\hbar n)^2 / (2mL^2)$. Here \hbar is Planck's constant; n is the quantum number; m is the mass of the particle. We obtain the derivative of $E_n(L)$ over L straightforwardly $\frac{dE_n}{dL} = -2 \frac{E_n(L)}{L}$.

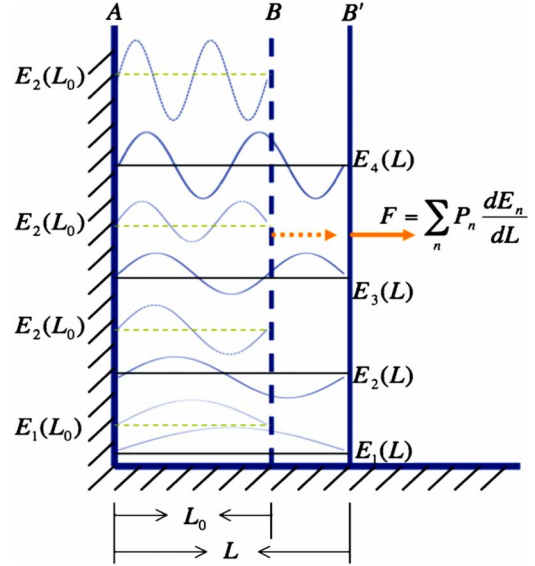


FIG. 1. (Color online) Schematic diagram of pressure in quantum-mechanical system (single particle in 1D box). One wall (A) of the square well is fixed, while the other one (B) is movable. The force acting on the wall B by the quantum system constrained in the potential well can be calculated from Eq. (3).

When the system is in thermal equilibrium with a heat bath at an inverse temperature $\beta = \frac{1}{kT}$, the force exerting on either wall of the potential can be calculated by substituting $\frac{dE_n}{dL}$ and the Gibbs distribution $P_n = \frac{1}{Z} e^{-\beta E_n}$ into Eq. (3). Here k is Boltzmann's constant and $Z = \sum_n e^{-\beta E_n}$ is the partition function. Alternatively, the expression of force (3) in a quantum-mechanical way can be obtained in a statistical-mechanical way [18],

$$\begin{aligned} F &= - \left(\frac{\partial \mathbb{F}}{\partial L} \right)_T = kT \left(\frac{\partial \ln Z}{\partial L} \right)_T = kT \frac{1}{Z} \frac{\partial}{\partial L} \sum_n e^{-\beta E_n} \\ &= - \sum_n \left(\frac{e^{-\beta E_n}}{Z} \right) \frac{\partial E_n}{\partial L} = - \sum_n P_n \frac{dE_n}{dL}, \end{aligned} \quad (4)$$

where $\mathbb{F} = -kT \ln Z$ is the free energy of the quantum system. It should be pointed out that Eq. (3) is more general than Eq. (4) because Eq. (3) stands no matter if the system is in equilibrium or not. When P_n in Eq. (3) satisfies Gibbs distribution $P_n = \frac{1}{Z} e^{-\beta E_n}$, or the system is in thermal equilibrium, the expectation value of force F of Eq. (3) reproduces the usual force in classical thermodynamics.

Another model example is the single particle in a 1D harmonic-oscillator potential (1DH) (see Fig. 2). Its Hamiltonian is the same as the Hamiltonian of a single-mode radiation field in a cavity [3]. For such a 1DH, we will see later that the definition of force (3) for a 1DH agrees with radiation pressure (4) of a single-mode radiation field. We would like to mention that the definition of force in Eq. (3) is a further step in quantum thermodynamics after the definitions of heat and work [Eq. (1)]. We will see that all these definitions of work, heat, entropy, and pressure for a quantum-

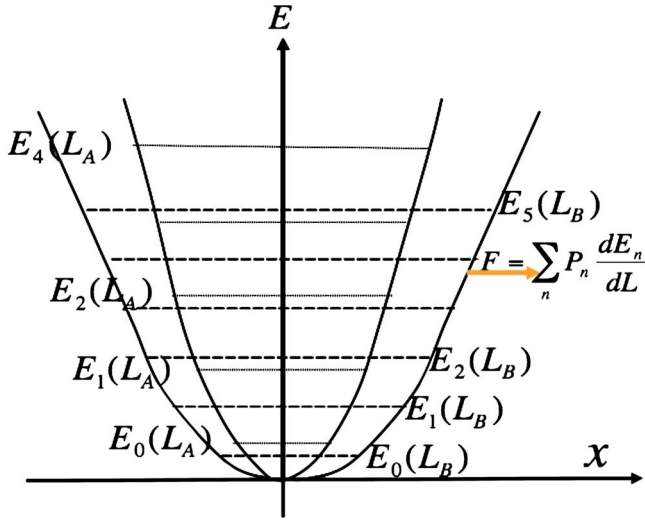


FIG. 2. (Color online) Radiation pressure of a single-mode radiation field. Here the width of the potential is inversely proportional to the mode frequency of the cavity $L \propto \frac{1}{\omega}$. The n th eigenenergy of the single-mode radiation field with the potential width L_α is given by $E_n(L_\alpha) = (n + \frac{1}{2}) \frac{\hbar s \pi c}{L_\alpha}$, $\alpha = A, B$. This pressure is equivalent to the pressure in a quantum-mechanical system—single particle in 1D harmonic oscillator. Hence quantum isobaric process based on single-mode radiation field is equivalent to that based on a 1D quantum harmonic oscillator.

mechanical system are self-consistent, and are consistent with classical thermodynamics.

B. Quantum isobaric process

Having clarified force for a quantum-mechanical system, in the following we study how to extend the classical isobaric process to a quantum-mechanical system. The classical isobaric process is a quasistatic thermodynamic process, in which the pressure of the system remains a constant [9,10]. The time scale of relaxation of the system with the heat bath is much shorter than the time scale of controlling the volume of the system [19]. In a classical isobaric process, in order to achieve a constant pressure, we must carefully control the temperature of the system, i.e., carefully control the temperature of the heat bath, when we change the volume of the classical system [10]. For example, for the classical ideal gas with the equation of state $PV = NkT$, the temperature of the system in the isobaric process is required to be proportional to the volume ($T \propto V$) of the gas so that the pressure can remain a constant. For a quantum-mechanical system, however, the change of the temperature of the heat bath with the generalized coordinate may not be so obvious as the classical ideal gas, because we usually do not know the equation of state of a quantum-mechanical system. Let us consider the quantum isobaric process based on a 1DB (see Fig. 1). For such a quantum-mechanical system, the pressure on the wall can be obtained from Eq. (3),

$$\begin{aligned} F &= - \sum_n P_n(L) \frac{dE_n(L)}{dL} = - \sum_n \frac{\exp[-\beta(L)E_n(L)] dE_n(L)}{Z(L) dL} \\ &= - \sum_n \frac{\exp[-\beta(L) \frac{\pi^2 \hbar^2 n^2}{2mL^2}]}{\frac{1}{2} \sqrt{\frac{2mL^2}{\pi \hbar^2 \beta(L)}}} \frac{(-2) \frac{\pi^2 \hbar^2 n^2}{2mL^2}}{L} \\ &= \frac{4}{L} \sqrt{\frac{\pi \hbar^2 \beta(L)}{2mL^2}} \left[- \frac{\partial}{\partial \beta(L)} \sum_n \exp\left(-\beta(L) \frac{\pi^2 \hbar^2 n^2}{2mL^2}\right) \right] \\ &= \frac{4}{L} \sqrt{\frac{\pi \hbar^2 \beta(L)}{2mL^2}} \left[- \frac{\partial}{\partial \beta(L)} \frac{1}{2} \sqrt{\frac{2mL^2}{\pi \hbar^2 \beta(L)}} \right] = \frac{1}{L\beta(L)}. \end{aligned} \quad (5)$$

Equation (5) can be regarded as the equation of state $FL = kT$ for the 1DB obtained from Eq. (3), and it means that if we want to keep the pressure F as a constant, we must control the temperature of the system to be proportional to the width of the potential well $\beta(L) = 1/(FL)$ when the system inside the box pushes one of the walls to perform work. This property of the 1DB is the same as the classical ideal gas. We will see more analogs between them later. It should be mentioned that the temperature function $\beta(L)$ of the “volume” in a quantum isobaric process is system dependent. In effect, for different quantum systems, the function of the temperature over the “volume” in the quantum isobaric process differs from one to another. In the following we consider the quantum isobaric process based on a single-mode radiation field in a cavity, which was first proposed as the working substance for a quantum heat engine in Ref. [3]. We assume that the cavity of length L and cross section A can support only a single mode of the field $\omega = \frac{s\pi c}{L}$, where s is an integer and c is the speed of light. The Hamiltonian reads

$$H = \sum_n (n + \frac{1}{2}) \hbar \omega |n\rangle \langle n|, \quad (6)$$

where $|n\rangle$ is the Fock state of the radiation field. From Eq. (3) we obtain the radiation force F as a function of the temperature β and the length of the cavity L [20],

$$\begin{aligned} F &= - \sum_n \frac{e^{-\beta(L)E_n(L)} dE_n(L)}{Z(L) dL} \\ &= - \frac{1}{1 - e^{-\beta(L)\hbar\omega}} \sum_n e^{-\beta(L)n\hbar\omega} \left[\left(n + \frac{1}{2} \right) \hbar \omega \right] \frac{1}{L} \\ &= \left[\frac{\hbar \frac{s\pi c}{L}}{e^{\beta(L)\hbar s\pi c/L} - 1} + \frac{1}{2} \hbar \frac{s\pi c}{L} \right] \frac{1}{L}. \end{aligned} \quad (7)$$

From Eq. (7) it can be inferred that in order to achieve a constant force, we must carefully control the temperature of the heat bath in the following subtle way:

$$\beta(L) = \frac{L}{\hbar s \pi c} \ln \frac{2FL^2 + \hbar s \pi c}{2FL^2 - \hbar s \pi c}. \quad (8)$$

It can be seen that in a quantum isobaric process, temperature function (8) for the single-mode radiation field is much more complicated than that $[\beta(L) \propto \frac{1}{L}]$ of a 1DB.

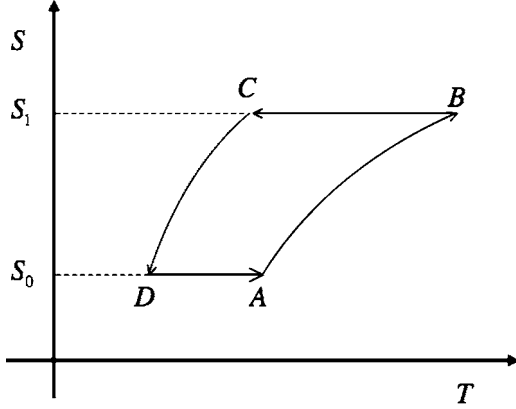


FIG. 3. Temperature-entropy T - S diagram of a quantum Brayton cycle (see Fig. 4) based on 1DB. In two adiabatic processes, $B \rightarrow C$ and $D \rightarrow A$, the entropy remains a constant.

For the convenience of later analysis, we would also like to calculate the entropy and the internal energy of the two systems in a quantum isobaric process. First we consider the 1DB. The entropy expression can be obtained from the above Eq. (1) [8],

$$S(L) = k_B \left\{ \frac{1}{2} + \ln \left[\frac{1}{2} \sqrt{\frac{2mL^2}{\pi \hbar^2 \beta(L)}} \right] \right\}. \quad (9)$$

Through the comparison with the entropy of a classical ideal gas [9,10], we find that the entropy of the classical ideal gas reproduces the entropy [Eq. (9)] of a 1DB if we choose the molecule number of the classical ideal gas to be $N=1$. We plot the entropy-temperature curve [Eq. (9)] of a quantum isobaric process in Fig. 3. The internal energy of the 1DB during the isobaric process can also be obtained analytically (the temperature of the heat bath is time dependent) as follows:

$$U(L) = - \sum_n \frac{e^{-\beta(L)E_n(L)}}{Z(L)} E_n(L) = \frac{1}{2\beta(L)}. \quad (10)$$

This expression of internal energy verifies the equipartition theorem [9] and justifies the result in Ref. [8] again: the internal energy of the 1DB depends only on the temperature. From Eqs. (9) and (10) we see that both the entropy and the internal energy of the 1DB have the same form as that of the classical ideal gas [9,10] if we choose the molecule number of the classical ideal gas to be $N=1$. Moreover, from Eq. (5) we know that the 1DB has the same equation of state $FL = kT$ as that of the classical ideal gas $PV = NkT$ except the difference of the particle number. Thus we conclude that the 1DB is the quantum-mechanical counterpart of the classical ideal gas. We would like to mention that in the study of the single-molecule engine by Szilard and Zurek [17], they simply employed the equation of state for the classical ideal gas $PV = Nk_B T$ and chose the particle number to be $N=1$. Nevertheless, this treatment may be questionable because the equation of state $PV = Nk_B T$ stands in the macroscopic and classical case. When we come to the extreme limit of a small system with only a few degrees of freedom, we must use the quantum-mechanical treatment as we present here. Fortu-

nately, all the treatments of the single-molecule engine [17] by Szilard and Zurek are in accordance with our quantum-mechanical treatments. Thus we say that our discussions lay the foundation for Szilard-Zurek single-molecule engine [17].

As to the single-mode radiation field, the entropy and the internal energy can be calculated as that in Ref. [3],

$$S(L) = \frac{\langle n \rangle \hbar \omega}{T} + k \ln(\langle n \rangle + 1), \quad (11)$$

$$U(L) = \sum_n \frac{e^{-\beta \hbar \omega}}{Z(L)} (n + \frac{1}{2}) \hbar \omega = (\langle n \rangle + \frac{1}{2}) \hbar \omega, \quad (12)$$

where $\langle n \rangle = [\exp(\hbar \omega / kT) - 1]^{-1}$ is the mean photon number.

It is easy to see that the entropy [Eq. (11)] and the internal energy [Eq. (12)] of a single-mode radiation field have different forms from that of the 1DB [Eqs. (9) and (10)], and thus from the classical ideal gas. The internal energy [Eq. (12)] of the single-mode radiation field depends on both the temperature β and the width L of the potential well, while the internal energy of the 1DB [Eq. (10)] depends on β only. In addition, the equation of state [Eq. (7)] of the single-mode radiation field differs from that [Eq. (5)] of the 1DB, and thus from the classical ideal gas. Based on these observations, we say that the single-mode radiation field has totally different thermodynamic properties from that of the classical ideal gas. It can be inferred that the quantum heat engine based on the single-mode radiation field can give us new results beyond that of the classical ideal gas. As we mentioned before, the Hamiltonian of the single-mode radiation field is the same as that of a 1DH. Thus all the results about the single-mode radiation field are the same as that for a 1DH. Alternatively, we can say that a 1DH is the counterpart of the single-mode photon gas, in analogy to the fact that a 1DB is the counterpart of the classical ideal gas. But it should be mentioned that the single-mode photon gas is still a quantum-mechanical system, while the classical ideal gas is a classical system. In the following we will alternatively use 1DH and single-mode photon gas.

In addition to our previous studies [8], up to now we have extended all four basic thermodynamic processes to the quantum-mechanical domain. For a comparison of quantum thermodynamics processes and their classical counterparts, see Table I.

III. QUANTUM BRAYTON CYCLE

In Sec. II, we extend the classical isobaric process to quantum-mechanical systems based on the definition of pressure [Eq. (3)]. In this section and Sec. IV, we study two kinds of thermodynamic cycles consisting of the quantum isobaric process, and compare them with their classical counterparts. We first consider the quantum Brayton cycle based on a 1DB. A quantum Brayton cycle is a quantum-mechanical analog of the classical Brayton cycle [9,10], which consists of two quantum isobaric processes and two quantum adiabatic processes. Similar to our discussion in Ref. [8], the counterpart of the classical adiabatic plus quasistatic process

TABLE I. Basic classical thermodynamic processes and their quantum counterparts. Here the classical thermodynamic processes are based on the classical ideal gas, while the quantum thermodynamic processes are based on the IDB. We illustrate the equations of state for the four basic thermodynamic processes, and we also indicate the invariant or varying variables in these processes. Here, we use “INV” to indicate the invariance of a thermodynamic quantity and “VAR” to indicate that it varies or changes.

	Isothermal ($T \equiv T_0$)	Isochoric ($V \equiv V_0$ or $L \equiv L_0$)	Isobaric ($P \equiv P_0$ or $F \equiv F_0$)	Adiabatic ($S \equiv S_0$)
Classical	$P(V)V = \text{const};$ VAR: S, V, P ; INV: T	$\frac{P(T)}{T} = \text{const};$ VAR: S, T, P ; INV: V	$\frac{V(T)}{T} = \text{const};$ VAR: S, T, V ; INV: P	$P(T)V^3(T) = \text{const};$ VAR: V, T, P ; INV: S
Quantum	$F(L)L = \text{const};$ VAR: E_n, P_n ; INV: T	$\frac{F(T)}{T} = \text{const};$ VAR: T, P_n ; INV: E_n	$\frac{L(T)}{T} = \text{const};$ VAR: T, E_n, P_n	$F(T)L^3(T) = \text{const};$ VAR: E_n, T ; INV: P_n

is the quantum adiabatic process [21]. In constructing the quantum Brayton cycle, we also require that (i) all the energy-level spacings of the work substance change by the same ratio in the quantum adiabatic process, and (ii) this ratio be equal to the ratio of the temperatures of the two heat baths just before and after the quantum adiabatic process. It should be mentioned that in the isothermal process of a Carnot cycle, the temperature of the heat bath is fixed. However, this is not the case in the isobaric process of a Brayton cycle. Hence, we cannot simply say that the ratio of the change of the energy-level spacings should be equal to the ratio of the temperatures of the two heat baths [8]. For the current example, it can be checked that the change of the energy-level spacings in the quantum adiabatic process (see Fig. 3) $B \rightarrow C$ and $D \rightarrow A$ should be equal to the ratio of temperatures of the heat baths at B and C , or at D and A (because $\frac{T_B}{T_C} = \frac{T_A}{T_D}$). Fortunately, the above condition (i) can be satisfied by some quantum-mechanical system, such as 1DB, 1DH, two-level system, etc., and our study will focus on these systems whose energy-level spacings change in the same ratio in the quantum adiabatic process. Otherwise, the irreversibility will arise [21]. We give a temperature-entropy T - S diagram of the quantum Brayton cycle (see Fig. 3). Through a standard procedure, we obtain (see Appendix A) the efficiency of the quantum Brayton cycle based on the 1DB,

$$\eta_{\text{Brayton}} = 1 - \left(\frac{F_0}{F_1}\right)^{2/3}, \tag{13}$$

where F_0 and F_1 are the pressures of the system during two quantum isobaric processes (see Fig. 4).

We would like to compare this efficiency of the quantum Brayton cycle [Eq. (13)] with its classical counterpart. From Eq. (9) we know that in the quantum adiabatic process ($S = \text{const}$), we have $TL^2 = \text{const}$. As a result the adiabatic exponent $\gamma = 3$ is obtained through the comparison with $TL^{\gamma-1} = \text{const}$ for the adiabatic process. Let us recall that the efficiency of a classical Brayton cycle is $\eta = 1 - \left(\frac{F_0}{F_1}\right)^{1-1/\gamma}$ [10], where γ is the classical adiabatic exponent. Thus our result [Eq. (13)] bridges the quantum Brayton cycle and classical Brayton cycle. Hence this justifies that the definition of pressure [Eq. (3)] for a quantum-mechanical system is self-consistent.

Similarly we obtain the efficiency of a quantum Brayton cycle based on the 1DH (see Appendix A),

$$\eta'_{\text{Brayton}} = 1 - \sqrt{\frac{F_0}{F_1}}. \tag{14}$$

From Eq. (11) we know that in a quantum adiabatic process $TL = \text{const}$. Thus $\gamma = 2$ for the 1DH is obtained. It can be seen that the efficiency of a quantum Brayton cycle obtained here [Eq. (14)] is the same as that of a classical Brayton cycle. Through the discussion of quantum Brayton cycles based on two model systems 1DH and 1DB, we see that the definition of pressure [Eq. (3)] for quantum systems has a clear physical implication, and our study bridges the thermodynamic cycles based on quantum and classical systems.

IV. QUANTUM DIESEL CYCLE

Except for the thermodynamic cycles consisting of two pairs of basic thermodynamic processes, such as the Carnot cycle, Otto cycle [8], and Brayton cycle, there are some interesting thermodynamic cycles consisting of more than two

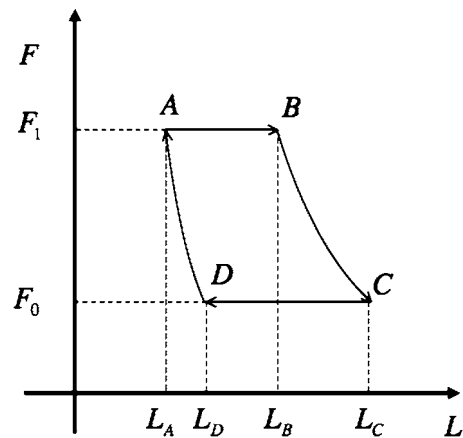


FIG. 4. Force-displacement F - L diagram of a quantum Brayton cycle based on a single particle in 1DB. $A \rightarrow B$ represents an isobaric expansion process with a constant force F_1 ; $B \rightarrow C$ represents an adiabatic expansion process with constant entropy S_1 ; $C \rightarrow D$ represents an isobaric compression process with constant pressure F_0 ; $D \rightarrow A$ is another adiabatic compression process with constant entropy S_0 .

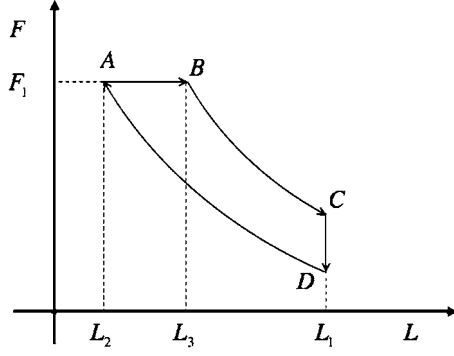


FIG. 5. Force-displacement F - L diagram of a quantum Diesel cycle based on 1DB and single-mode radiation field. $A \rightarrow B$ represents an isobaric expansion process with a constant pressure F_1 ; $B \rightarrow C$ represents an adiabatic expansion process with constant entropy; $C \rightarrow D$ represents an isochoric compression process with constant volume L_1 ; $D \rightarrow A$ is another adiabatic compression process.

kinds of thermodynamic processes, such as the Diesel cycle. The Diesel cycle consists of two adiabatic processes, one isobaric process, and one isochoric process [10] (see Fig. 5). In order to construct such a quantum Diesel cycle, we require (1) the quantum adiabatic conditions are satisfied, and (2) all energy-level spacings change in the same ratio in the thermally isolated process [21] because this is the quantum counterpart of the classical adiabatic process (thermally isolated plus quasistatic process) [21]. Besides, the ratio of the change of the energy-level spacings in the quantum adiabatic process $D \rightarrow A$ should be equal to the ratio $\frac{T_A}{T_D}$ of the temperatures of the heat bath at A and at D (see Fig. 5); the energy-level spacing at C should be equal to that at point D (see Fig. 5).

In the following we will consider implementing the quantum Diesel cycle in a 1DB and in 1DH. First we consider the 1DB. The efficiency of a quantum Diesel cycle based on 1DB can be obtained through a straightforward calculation (see Appendix B),

$$\eta_{\text{Diesel}} = 1 - \frac{1}{3} \frac{r_E^3 - r_C^3}{r_E - r_C} = 1 - \frac{1}{3} (r_E^2 + r_C r_E + r_C^2). \quad (15)$$

Here $r_C \equiv \frac{L_2}{L_1}$ (see Fig. 5) and $r_E \equiv \frac{L_3}{L_1}$ (see Fig. 5) are the compression and expansion ratios of the volumes. This efficiency for a quantum Diesel cycle based on a 1DB agrees with that of a classical Diesel cycle, too. Through a similar analysis we obtain the efficiency for a quantum Diesel cycle based on a 1DH with the only change of γ from 3 in Eq. (15) to 2,

$$\eta'_{\text{Diesel}} = 1 - \frac{1}{2} \frac{r_E^2 - r_C^2}{r_E - r_C} = 1 - \frac{1}{2} (r_E + r_C). \quad (16)$$

Before concluding this section, we would like to mention that we can also discuss the quantum Brayton cycle and the quantum Diesel cycle based on an arbitrary quantum system, such as the three-dimensional (3D) black body radiation field or a spin-1/2 system in an external magnetic field with the Hamiltonian $H = \frac{1}{2} B \sigma_z$. Here σ_z is the Pauli matrix and B is

the external magnetic field. It can be seen from Table II that the efficiencies for both the quantum Carnot cycle and classical Carnot cycle are always equal to the Carnot efficiency $1 - \frac{T_C}{T_H}$ irrespective of the properties of the working substance. Different from the Carnot cycle, the efficiencies of the Otto cycle, Brayton cycle, and Diesel cycle are working substance dependent (see Table II). More specifically, they depend on the adiabatic exponent γ of the working substance. As long as we get the adiabatic exponent γ of the quantum system, we obtain the explicit expression of the efficiencies of the quantum thermodynamic cycles by substituting γ into the expression of the efficiencies of the classical thermodynamics with their adiabatic exponent. For example, for a spin-1/2 system in an external magnetic field, we choose the inverse of the magnetic field strength as the generalized coordinate $L = \frac{1}{B}$. Then it can be found that the adiabatic exponent for such a system is $\gamma = 2$. As a result, the efficiencies of a quantum Brayton cycle and a quantum Diesel cycle based on a spin-1/2 system in an external magnetic field are the same as that based on a 1DH [Eqs. (14) and (16)]. Similarly, the efficiencies for a Brayton cycle and a Diesel cycle based on a 3D radiation field can be obtained straightforwardly by substituting γ with the adiabatic exponent $\frac{4}{3}$ [9,10] for the 3D radiation field. In Table II we list the working efficiencies for several typical thermodynamic cycles based on different kinds of classical and quantum working substances (based on their adiabatic exponent).

V. CONCLUSIONS AND REMARKS

In summary, in this paper, we study the quantum-mechanical analogy of the classical isobaric process based on a microscopic definition of force. In studying the thermodynamic properties of a small quantum system, we use a new pair of conjugate variables P_n and E_n instead of the usual thermodynamic variables P and V or T and S [23]. The general expression of force for an arbitrary quantum system $F = -\sum_n P_n \frac{dE_n(L)}{dL}$ is found. It can be checked that this expression is in accordance with the force $F = -(\frac{\partial E}{\partial L})_T$ in statistical mechanics if the quantum system is in thermal equilibrium with a heat bath. In addition we clarify the relation between the adiabatic process (thermally isolated plus quasistatic process) for classical systems and the quantum adiabatic process in quantum systems. Based on quantum isobaric processes, we make a quantum-mechanical extension of some typical thermodynamic cycles. The properties of these quantum thermodynamic processes and cycles are clarified, and we bridge the quantum thermodynamic cycles and their classical counterparts. The quantum heat engines and their classical counterparts have the same efficiencies as long as their working substance has the same adiabatic exponent. The definitions of force and work for a single-particle quantum system may have important application in the experimental exploration of nonequilibrium thermodynamics in small quantum systems, such as the quantum Jarzynski equality and quantum Crooks fluctuation theorem [2,24]. Though the working substance of quantum heat engines deviates from the thermodynamic limit, we reproduce the efficiency of classical heat engines.

TABLE II. Working efficiencies of typical classical thermodynamic cycles and their quantum counterparts based on different kinds of working substance. It can be seen that (1) except the Carnot cycle, the efficiencies of all the thermodynamic cycles are working substance dependent, and (2) both quantum thermodynamic cycles and classical thermodynamic cycles have the same efficiency as long as the adiabatic exponent is the same. Adiabatic exponents for monoatomic, diatomic, and polyatomic classical idea gases can be found in [22]. Here T_C and T_H are the temperatures of the cold and hot reservoirs; $V_0(L_0, S_0)$ and $V_1(L_1, S_1)$ are the volume (length, area) of the working substance in two isochoric processes; $P_0(F_0)$ and $P_1(F_1)$ are the pressure (force) of the working substance in the two isobaric processes.

		Carnot (two isothermal + two adiabatic) $\eta = 1 - \frac{T_C}{T_H}$	Otto (two isobaric + two adiabatic) $\eta = 1 - (\frac{V_0}{V_1})^{\gamma-1}$	Brayton (two isobaric + two adiabatic) $\eta = 1 - (\frac{P_0}{P_1})^{1-1/\gamma}$	Diesel (isochoric + isobaric + two isobaric) $\eta = 1 - \frac{1}{\gamma} \frac{(\frac{V_2}{V_1})^\gamma - (\frac{V_3}{V_1})^\gamma}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
Classical	Monoatomic classical ideal gas ($\gamma = \frac{5}{3}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{2/3}$	$\eta = 1 - (\frac{P_0}{P_1})^{2/5}$	$\eta = 1 - \frac{3}{5} \frac{(\frac{V_2}{V_1})^{5/3} - (\frac{V_3}{V_1})^{5/3}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
	Diatomic classical ideal gas ($\gamma = \frac{7}{5}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{2/5}$	$\eta = 1 - (\frac{P_0}{P_1})^{2/7}$	$\eta = 1 - \frac{5}{7} \frac{(\frac{V_2}{V_1})^{7/5} - (\frac{V_3}{V_1})^{7/5}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
	Polyatomic classical ideal gas ($\gamma = \frac{4}{3}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{1/3}$	$\eta = 1 - (\frac{P_0}{P_1})^{1/4}$	$\eta = 1 - \frac{3}{4} \frac{(\frac{V_2}{V_1})^{4/3} - (\frac{V_3}{V_1})^{4/3}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
Quantum	Single particle in 1D box ($\gamma = 3$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{L_0}{L_1})^2$	$\eta = 1 - (\frac{F_0}{F_1})^{2/3}$	$\eta = 1 - \frac{1}{3} \frac{(\frac{L_2}{L_1})^3 - (\frac{L_3}{L_1})^3}{(\frac{L_2}{L_1}) - (\frac{L_3}{L_1})}$
	Single particle in 2D box ($\gamma = 2$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - \frac{S_0}{S_1}$	$\eta = 1 - (\frac{P_0}{P_1})^{1/2}$	$\eta = 1 - \frac{1}{2} (\frac{S_2}{S_1} - \frac{S_3}{S_1})$
	Single particle in 3D box ($\gamma = \frac{5}{3}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{2/3}$	$\eta = 1 - (\frac{P_0}{P_1})^{2/5}$	$\eta = 1 - \frac{3}{5} \frac{(\frac{V_2}{V_1})^{5/3} - (\frac{V_3}{V_1})^{5/3}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
	1D single-mode photon field ($\gamma = 2$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - \frac{L_0}{L_1}$	$\eta = 1 - (\frac{F_0}{F_1})^{1/2}$	$\eta = 1 - \frac{1}{2} (\frac{L_2}{L_1} - \frac{L_3}{L_1})$
	3D black body radiation field ($\gamma = \frac{4}{3}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{1/3}$	$\eta = 1 - (\frac{P_0}{P_1})^{1/4}$	$\eta = 1 - \frac{3}{4} \frac{(\frac{V_2}{V_1})^{4/3} - (\frac{V_3}{V_1})^{4/3}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
	1D harmonic oscillator ($\gamma = 2$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - \frac{L_0}{L_1}$	$\eta = 1 - (\frac{F_0}{F_1})^{1/2}$	$\eta = 1 - \frac{1}{2} (\frac{L_2}{L_1} - \frac{L_3}{L_1})$
	2D harmonic oscillator ($\gamma = \frac{3}{2}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{S_0}{S_1})^{1/2}$	$\eta = 1 - (\frac{P_0}{P_1})^{1/3}$	$\eta = 1 - \frac{2}{3} \frac{(\frac{S_2}{S_1})^{3/2} - (\frac{S_3}{S_1})^{3/2}}{(\frac{S_2}{S_1}) - (\frac{S_3}{S_1})}$
	3D harmonic oscillator ($\gamma = \frac{4}{3}$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - (\frac{V_0}{V_1})^{1/3}$	$\eta = 1 - (\frac{P_0}{P_1})^{1/4}$	$\eta = 1 - \frac{3}{4} \frac{(\frac{V_2}{V_1})^{4/3} - (\frac{V_3}{V_1})^{4/3}}{(\frac{V_2}{V_1}) - (\frac{V_3}{V_1})}$
	Spin-1/2 (2-level system) ($\gamma = 2$)	$\eta = 1 - \frac{T_C}{T_H}$	$\eta = 1 - \frac{L_0}{L_1}$	$\eta = 1 - (\frac{F_0}{F_1})^{1/2}$	$\eta = 1 - \frac{1}{2} (\frac{L_2}{L_1} - \frac{L_3}{L_1})$

Hence our study lays the concrete foundation for the Szilard-Zurek single-molecule engine. Moreover, we found the close relation between a classical ideal gas and IDB, and between a single-mode photon gas and IDH.

Before concluding this paper, we would like to mention that in our current study we focus on the quantum single-particle system and its related quantum-mechanical generalization of heat, work, and pressure, and we regain the results of classical thermodynamic processes and cycles. We also notice some studies about quantum heat engines with a quan-

tum many-body system as the working substance [25]. For a quantum many-body system, e.g., ideal bosonic gas or ideal fermionic gas, the mechanical variables, such as heat, work, and pressure, are well defined and their equation of state as well as their expression of internal energy [18] deviate from that of the classical ideal gas. As a result, the properties of quantum thermodynamic cycles based on the quantum many-body system deviate from that of the classical ideal gas due to quantum degeneracy. Finally, similar to the discussion about finite-power Carnot engine [26], we can discuss the

finite-time quantum Brayton cycle and quantum Diesel cycle. Finite-power analysis of the Brayton cycle and Diesel cycle will be given later.

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APPENDIX A: OPERATION EFFICIENCY OF QUANTUM BRAYTON CYCLE

According to the definition of heat exchange [Eq. (1)] in the quantum-mechanical system, we obtain the heat absorbed by the system from a time-dependent heat bath during the quantum isobaric expansion process $A \rightarrow B$ (see Figs. 3 and 4),

$$\begin{aligned} dQ_{AB} &= \int_{L_A}^{L_B} \left[\sum_n E_n(L) \frac{dP_n(L)}{dL} \right] dL \\ &= \sum_n \int_{L_A}^{L_B} \left[[E_n(L)P_n(L)]' - \frac{dE_n(L)}{dL} P_n(L) \right] dL \\ &= \sum_n [E_n(L_B)P_n(L_B) - E_n(L_A)P_n(L_A)] + \int_{L_A}^{L_B} F(L) dL \\ &= \frac{1}{2} [F_1 L_B - F_1 L_A] + F_1 (L_B - L_A) = \frac{3}{2} F_1 (L_B - L_A). \end{aligned} \quad (\text{A1})$$

In obtaining the above result we have used Eqs. (5) and (10). Similarly, we obtain the heat released to the time-dependent entropy sink,

$$dQ_{CD} = \frac{3}{2} F_0 (L_C - L_D). \quad (\text{A2})$$

Hence, the efficiency of the quantum Brayton cycle based on a 1DB can be expressed as

$$\eta_{\text{Brayton}} = 1 - \frac{F_0 (L_C - L_D)}{F_1 (L_B - L_A)}. \quad (\text{A3})$$

Due to the equation of motion [Eq. (5)] and the expression of the internal energy [Eq. (10)], we have $F_1 \times L_B / 2 = U(L_B)$, $F_0 \times L_C / 2 = U(L_C)$. In addition to the relation of the internal energies in the quantum adiabatic process $B \rightarrow C$

$$\frac{U(L_B)}{U(L_C)} = \left(\frac{L_C}{L_B} \right)^2, \quad (\text{A4})$$

we have

$$\frac{F_1}{F_0} = \left(\frac{L_C}{L_B} \right)^3 \quad (\text{A5})$$

for the quantum adiabatic process $B \rightarrow C$. Through a similar analysis we obtain

$$\frac{F_1}{F_0} = \left(\frac{L_D}{L_A} \right)^3 \quad (\text{A6})$$

for another quantum adiabatic process $D \rightarrow A$. Based on all the above results [Eqs. (A3), (A5), and (A6)], we obtain the efficiency of the quantum Brayton cycle based on the 1DB,

$$\eta_{\text{Brayton}} = 1 - \left(\frac{F_0}{F_1} \right)^{2/3}. \quad (\text{A7})$$

In the following we consider a quantum Brayton cycle based on the 1DH. Similar to the above analysis, we calculate the heat absorbed by the system during the quantum isobaric expansion process $A \rightarrow B$ (see Fig. 3)

$$\begin{aligned} dQ_{AB} &= \int_{L_A}^{L_B} \left[\sum_n E_n(L) \frac{dP_n(L)}{dL} \right] dL \\ &= [U(L_B) - U(L_A)] + \int_{L_A}^{L_B} F d(L) \\ &= \left(\frac{\hbar \omega_B}{e^{\beta(L_B) \hbar \omega_B} - 1} + \frac{\hbar \omega_B}{2} \right) \\ &\quad - \left(\frac{\hbar \omega_A}{e^{\beta(L_A) \hbar \omega_A} - 1} + \frac{\hbar \omega_A}{2} \right) + F_H (L_B - L_A) \\ &= F_1 (L_B - L_A), \end{aligned} \quad (\text{A8})$$

where we have used relations (7) and (12) in the quantum isobaric process ($A \rightarrow B$). Similarly, we obtain the heat released to the entropy sink in another quantum isobaric process $C \rightarrow D$,

$$dQ_{CD} = F_0 (L_C - L_D). \quad (\text{A9})$$

The efficiency of the quantum Brayton cycle based on a 1DH can be expressed as

$$\eta'_{\text{Brayton}} = 1 - \frac{F_0 (L_C - L_D)}{F_1 (L_B - L_A)}. \quad (\text{A10})$$

From Eqs. (7) and (12) we have $F_1 \times L_B = U(L_B)$ and $F_0 \times L_C = U(L_C)$. In addition to the relation of internal energy in the quantum adiabatic process

$$\frac{U(L_B)}{U(L_C)} = \frac{L_C}{L_B}, \quad (\text{A11})$$

we have

$$\frac{F_1}{F_0} = \left(\frac{L_C}{L_B} \right)^2. \quad (\text{A12})$$

Hence, from Eqs. (A10) and (A12) we obtain the efficiency of a quantum Brayton cycle based on a 1DH,

$$\eta'_{\text{Brayton}} = 1 - \sqrt{\frac{F_0}{F_1}}. \quad (\text{A13})$$

APPENDIX B: OPERATION EFFICIENCY OF QUANTUM DIESEL CYCLE

For a quantum Diesel cycle (see Fig. 5), the input energy in the quantum isobaric process $A \rightarrow B$ and the output energy

in the quantum isochoric process $C \rightarrow D$ can be calculated as

$$Q_{\text{in}} = C_P(T_B - T_A),$$

$$Q_{\text{out}} = C_V(T_C - T_D), \quad (\text{B1})$$

where C_P and C_V are the heat capacity at constant pressure and constant volume, respectively; T_A , T_B , T_C , and T_D are the temperatures of the system at different points of the Diesel cycle (see Fig. 5). Thus the efficiency of the quantum Diesel cycle can be expressed in terms of heat capacities and temperatures,

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{C_V(T_C - T_D)}{C_P(T_B - T_A)}. \quad (\text{B2})$$

It is convenient to express this efficiency [Eq. (B2)] in terms of compression ratio $r_C \equiv \frac{L_2}{L_1}$ (see Fig. 5) and expansion ratio $r_E \equiv \frac{L_3}{L_1}$ (see Fig. 5) of the volumes. Now using the equation of state $FL = kT$ [Eq. (5)] and $\frac{C_P}{C_V} = \gamma = 3$ for a 1DB, the efficiency [Eq. (B2)] can be rewritten as

$$\eta = 1 - \frac{1}{3} \frac{(F_C L_C - F_D L_D)}{(F_B L_B - F_A L_A)}. \quad (\text{B3})$$

By utilizing the facts $L_C = L_D = L_1$ and $F_A = F_B = F_1$ (see Fig. 5), we further simplify Eq. (B3) to

$$\eta = 1 - \frac{1}{3} \frac{L_1(F_C - F_D)}{F_1(L_B - L_A)} = 1 - \frac{1}{3} \frac{\left(\frac{F_C}{F_1} - \frac{F_D}{F_1}\right)}{(r_E - r_C)}. \quad (\text{B4})$$

Finally by making use of the adiabatic condition $FL^3 = \text{const}$ for a 1DB in the quantum adiabatic process, we obtain

$$\frac{F_C}{F_1} = \left(\frac{L_3}{L_1}\right)^3 = r_E^3,$$

$$\frac{F_D}{F_1} = \left(\frac{L_2}{L_1}\right)^3 = r_C^3. \quad (\text{B5})$$

Substituting Eq. (B5) into Eq. (B4), the efficiency of a quantum Diesel cycle based on a 1DB can be written as

$$\eta_{\text{Diesel}} = 1 - \frac{1}{3} \frac{r_E^3 - r_C^3}{r_E - r_C} = 1 - \frac{1}{3} (r_E^2 + r_C r_E + r_C^2). \quad (\text{B6})$$

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- [21] In the classical thermodynamic cycles, the adiabatic process implies (1) thermally isolated and (2) quasistatic, or very slow [9,15]. If the thermally isolated process proceeds fast, the quasistatic conditions are not satisfied. As a result, there will be an internal entropy increase, and irreversibility arises. In order to construct a reversible cycle, such as the Carnot cycle and Brayton cycle, the quasistatic condition must be satisfied in the thermally isolated process. Similarly, for a quantum thermodynamic cycle, the quantum-mechanical counterpart of the classical adiabatic process implies (1) thermally isolated and (2) no interstate excitations [8] and (3) all energy-level spacings change in the same ratio. Alternatively, the quantum-mechanical counterpart of the adiabatic process is the quantum adiabatic process given that all energy-level spacings change in the same ratio. This is because if one starts from a Gibbs density operator, when the quantum adiabatic conditions are satisfied and all energy-level spacings change in the same ratio as we change a parameter of the Hamiltonian, it will remain Gibbsian, so there is no source of irreversibility. On the contrary, if either (1) the quantum adiabatic conditions are not satisfied, or (2) the energy-level spacings do not change in the same ratio in the thermally isolated process, the density operator will not remain Gibbsian, and irreversibility arises. Hence, in order to construct a reversible quantum thermodynamic cycle (quantum-mechanical counterpart of reversible classical thermodynamic cycles), we must focus on those systems whose energy-level spacings change in the same ratio and use the quantum adiabatic process to replace the classical adiabatic plus quasistatic process.
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