Chemical Physics 494 (2017) 47–55

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Irreversible thermodynamic analysis and application for molecular heat engines

Umberto Lucia [a,*], Emin Açıkkalp [b]

[a] Dipartimento Energia "Galileo Ferraris", Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[b] Department of Mechanical and Manufacturing Engineering, Engineering Faculty, Bilecik S.E. University, Bilecik 11210, Turkey

ARTICLE INFO

Article history:
Received 3 June 2017
In final form 30 July 2017
Available online 1 August 2017

Keywords:
Molecular heat engines
Irreversibility
Finite time thermodynamics
Quantum heat engine
Quantum constructal law
Non-equilibrium thermodynamics

ABSTRACT

Is there a link between the macroscopic approach to irreversibility and microscopic behaviour of the systems? Consumption of free energy keeps the system away from a stable equilibrium. Entropy generation results from the redistribution of energy, momentum, mass and charge. This concept represents the essence of the thermodynamic approach to irreversibility. Irreversibility is the result of the interaction between systems and their environment. The aim of this paper is to determine lost works in a molecular engine and compare results with macro (classical) heat engines. Firstly, irreversible thermodynamics are reviewed for macro and molecular cycles. Secondly, irreversible thermodynamics approaches are applied for a quantum heat engine with -1/2 spin system. Finally, lost works are determined for considered system and results show that macro and molecular heat engines obey same limitations. Moreover, a quantum thermodynamic approach is suggested in order to explain the results previously obtained from an atomic viewpoint.

1. Introduction

Applications of thermodynamics range from the thermoeconomic evaluation of the energy resources, to the relationships among properties of matter, living matter included. Energy is a thermodynamic property, and it is always constant in the universe; it doesn't destroy, but only changes form a form to another one [1]. The useful work is obtained by evaluating the variations of the energy, which means that any change in a system is always related to a transition between, at least, two different system states.

Energy changes, no more than a conversion form one form of energy to another one, and interactions with environment are fully explained by the laws of thermodynamics. The first law of thermodynamics expresses the conservation of energy, while the second law states that entropy continuously increases for the system and its environment [2]. The second law gives us information about the quality of the energy and the evolution path of the system, as well as it allows us to evaluate the irreversibility of any real system [1]. Scientists and engineers have always been trying to obtain the maximum useful work and to decrease losses or irreversibility to the minimum level related to the specific constraints [3–26].

During the last decades, a continuous interest on micro- and nano-thermodynamic cycles is growing, with developments in nano-technology and nano-medicine. Thermodynamic assessments for quantum- and nano-systems, hence quantum thermodynamics, has been focused on [27–75]. In recent years, thermodynamic developments in the field of nanotechnology have raised novel questions about thermodynamics away from the thermodynamic limit. Indeed, quantum heat engines are devices that convert heat into work described by the laws of quantum and statistical thermodynamics. They have been a subject of intense research due to their great practical applications, as, for example:

1. Different thermometry approach, with the aim to reduce the dimensions of the probe and in pushing away from the thermalisation timescale to obtain a temperature measurement response in the emergence of small thermometers for nano-scale use;
2. The use in opto-mechanical systems, for the realization of nano-scale quantum thermal machines with particular interest for nano-mechanical resonators and quantum opto-mechanical engines, which should convert incoherent thermal energy into coherent mechanical work for power applications in photo-voltaic systems;
3. The bacteria conversion of light energy into bio-fuels;

* Corresponding author.
E-mail addresses: umberto.lucia@polito.it (U. Lucia), eacikkalp@gmail.com (E. Açıkkalp).

http://dx.doi.org/10.1016/j.chemphys.2017.07.009
0301-0104/

and many others. Unlike a classical heat engine, in quantum heat engines, the energy exchanged between the system and the thermal reservoirs occurs in quantized fashion. Therefore the quantum heat engines are modelled as sets having discrete energy levels unlike classical engines. But, one of the open problems of this topic is the link between classical and quantum thermodynamics for the analysis and designing of the quantum heat engines.

In 1803, Lazare Carnot developed a mathematical analysis of the efficiency of pulleys and inclined planes [76] in a general discussion on the conservation of mechanical energy. He highlighted that, in any movement, there always exists a loss of "moment of activity". In 1824, his son Sadi Carnot [3] introduced the concept of the ideal engine. It is a system which operates on a completely reversible cycle without any dissipation. But, this result seems nonsensical because, apparently, this system has no irreversibility and, consequently, it could convert all the absorbed heat into work, without any energy loss. On the contrary, Carnot proved that [3,4]:

1. All ideal engines operating between the same two thermal baths of temperature T_1 and T_2, with $T_1 > T_2$, has the same efficiency $\eta_C = 1 - T_1/T_2$;
2. Any other engine has an efficiency η such that always $\eta < \eta_C$.

Consequently, the efficiency of a reversible Carnot cycle is the upper bound of thermal efficiency for any heat engine working between the same temperature limits [3,4,17,76]. Carnot's general conclusion on heat engines is no more than the proof of the existence of natural limit for the conversion rate of the heat into the mechanical energy [4].

A great number of attempts have been developed to improve the calculation of the efficiency of the real machine [5,17,77–85] because all the thermodynamic processes occur in finite-size devices and in finite-time, in presence of irreversibility. The Carnot's limit is inevitable for any natural system [4], and it has always been experimentally verified.

In this paper, it is aimed to determine irreversibility in a quantum heat engine. Irreversibility is classified external, internal and total irreversibility that is sum of internal and external irreversibility. A method is presented to describe irreversibility for a quantum heat engine operating -1/2 spin system and also some numerical result are summarized.

2. Irreversibility from a quantum point of view

In This Section we consider the continuous interaction between atomic electrons and the environment photons. For simplicity, but without any loss of generality, we consider the Hydrogen-like atoms in interaction with the electromagnetic waves present in their environment.

The electromagnetic wave is a flow of photons, which incomes into the atoms, are absorbed by the atomic electrons if the electromagnetic wave frequency is resonant, and outcomes from them. At atomic level, the photons can be absorbed by the electrons of the atoms, and an electronic energy transition occurs between energy levels of two atomic stationary states. Then, the photons are emitted by the excited electrons, when they jump down into the energy level of the original stationary state.

Apparently, there are no changes in the energy of the atom, but only in the electronic transition. But, in reality there exists a change in the kinetic energy of the center of mass of the atom, which is usually negligible in relation to the to the energy change in electronic transition. Moreover, the time of occurrence of the energy variation of the atomic center of mass (10^{-13} s) is greater than the time of electronic transition (10^{-15} s).

Here, we stress that an energy variation of the atomic center of mass exists and it cannot be neglected if we consider a great number of interaction as it happens at macroscopic level [86].

Any atomic stationary state has a well defined energy level, identified by the principal quantum number n [87–94]. An electronic transition between two energy levels can occur following the quantum selection rule $\Delta n = n_f - n_i = \pm 1$ [87–94], where the subscript f means final state and the subscript i means initial state. The atom has an atomic number Z and only one electron in the last orbital. This electron moves in its orbital, for which, following the approach used in spectroscopy [92–95], we can introduced [86]:

1. The apparent atomic radius:

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e Z e^2}\, n^2 \tag{1}$$

2. The energy of the atomic level:

$$E_n = \frac{m_e Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} \tag{2}$$

3. the Sommerfeld-Wilson rule states that [38–41]:

$$\oint p_e dr_n = p_e r_n = m_e v_e r = n\hbar \tag{3}$$

where p_e r is the angular momentum of the electron, being r_n defined by the relation (1), $n = 1, 2, 3, \ldots$ is the principal quantum number, always integer, and $\hbar$ is the Dirac constant, $p_e = m_e v_e$ is the electronic momentum, where m_e is the mass of the electron and v_e its velocity inside the atom, e is the elementary charge, and ε_0 is the electric permittivity. Considering an Hydrogen-like atom, at initial state, the geometric reference system can be fixed in the center of mass of the nucleus, so that the atom is at rest with null momentum $\mathbf{p}_{atm}$. Its Schrödinger's equation is [87–95]:

$$\left[-\frac{\hbar^2}{2m_N}\nabla^2_{\mathbf{r}_N} - \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_e} + V(\mathbf{r}_e - \mathbf{r}_N)\right]\psi(\mathbf{r}_N, \mathbf{r}_e) = E_{tot}\psi(\mathbf{r}_N, \mathbf{r}_e) \tag{4}$$

where $\hbar$ is the Dirac constant, m_N is the mass of the nucleus, m_e is the mass of the electron, $\mathbf{r}_N$ is the nucleus coordinate, $\mathbf{r}_e$ is the electron coordinate, $V(\mathbf{r}_e - \mathbf{r}_N)$ is the electrostatic potential, E_{tot} is the total energy, and $\psi(\mathbf{r}_N, \mathbf{r}_e)$ is the wave function. Now, by using the relative coordinates $\mathbf{r} = \mathbf{r}_N - \mathbf{r}_e$, the coordinates of the center of mass$\mathbf{R} = (m_N\mathbf{r}_N + m_e\mathbf{r}_e)/(m_N + m_e)$, the total mass $M = m_N + m_e$, the reduced mass $\mu = (m_N^{-1} + m_e^{-1})^{-1}$, the momentum of the center of mass $\mathbf{P} = M\dot{\mathbf{R}} = -i\hbar\nabla_{\mathbf{R}}$, and momentum of the reduced mass particle $\mathbf{p} = \mu\dot{\mathbf{r}} = -i\hbar\nabla_{\mathbf{r}}$, the Eq. (4) becomes [87–95]:

$$\left[\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right) - \frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\right]\psi(\mathbf{r}, \mathbf{R}) = E_{tot}\psi(\mathbf{r}, \mathbf{R}) \tag{5}$$

The wave function $\psi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{r})\vartheta(\mathbf{R})$ is usually introduced to separate the Eq. (5) in the following two equations:

$$\begin{aligned} &-\tfrac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\vartheta(\mathbf{R}) = E_{CM}\vartheta(\mathbf{R}) \\ &\left(-\tfrac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right)\phi(\mathbf{r}) = E_\mu\phi(\mathbf{r}) \end{aligned} \tag{6}$$

where $E_{CM} = \boldsymbol{P}^2/2M$ is the energy of the free particle *center of mass*, and E_μ is the energy of the bound particle of *reduced mass*, such that $E_{tot} = E_{CM} + E_\mu$, and $V(\mathbf{r}) = -Ze^2/r$.

Now, we consider the Hydrogen-like atom in interaction with external electromagnetic waves. The electromagnetic radiation is a flux of photons, with [95,96]:

1. The energy E_γ:

$$E_\gamma = h\nu \tag{7}$$

where h is the Planck's constant (6.62607×10^{-34} J s), and ν is the frequency of the electromagnetic wave;

2. The momentum p_γ:

$$p_\gamma = \frac{h\nu}{c} \tag{8}$$

We define the thermodynamic control volume as the sphere with center in the center of mass of the atomic nucleus and radius defined by the relation (1) with $n+1$ instead of n. Consequently, the interaction between the electromagnetic radiation and the Hydrogen-like atom can be analysed as the interaction between the flux of photons with an open system (the atom of principal quantum number n), through the border of the control volume defined by the sphere of radius:

$$r = \frac{4\pi\varepsilon_0\hbar^2}{m_e Z e^2}\,(n+1)^2 \tag{9}$$

with center in the center of the atomic nucleus. The atomic electron absorbs the incoming photon when its frequency ν is the resonant frequency, required by the transition between the initial E_i and final E_f energy levels [87–96], corresponding to the quantized energy:

$$\nu = \frac{E_f - E_i}{h} \tag{10}$$

where h is the Planck's constant. Emission of the this photon results in the reverse process.

The momentum of the incoming photon is $h\nu\ \mathbf{u}_c/c$, where $\mathbf{u}_c$ is the versor of propagation of the electromagnetic wave, and c is the velocity of light in vacuum. When an electron absorbs the incoming photon, the atomic momentum becomes [87–96]:

$$\mathbf{p}_{atm} = -\frac{h\nu}{c}\,\mathbf{u}_c \tag{11}$$

and the electron undergoes an energy levels transition, from the stationary state of energy E_i to the stationary state of energy E_f, which results [86]:

$$E_f = E_i + h\nu - \frac{p_{atm}^2}{2M} = E_i + h\nu - \frac{(h\nu)^2}{2Mc^2} \tag{12}$$

where ${p^2}_{atm}/2M$ is the kinetic energy gained by the atom, and M is the mass of the atom. So, we can obtain [86–96]:

$$h\nu = \frac{(E_f - E_i)}{1 - \frac{h\nu}{2Mc^2}} \tag{13}$$

In a similar way, for the emission of a photon, we can obtain [86–96]:

$$h\nu = \frac{(E_i - E_f)}{1 + \frac{h\nu}{2Mc^2}} \tag{14}$$

As a consequence of the absorption of the photon, the laws of conservation of momentum and energy due to the absorption of the photon, hold to [86–96]:

$$\begin{aligned}
&\mathbf{P}' = M\dot{\mathbf{R}}'\\
&\mathbf{p}' = \mu\dot{\mathbf{r}}'\\
&\dot{\mathbf{r}}' = \dot{\mathbf{r}}'_e - \dot{\mathbf{r}}_N = \tfrac{\mathbf{p}'_e}{m_e} - \tfrac{\mathbf{p}_N}{m_N} = \tfrac{m_N\mathbf{p}'_e - m_e\mathbf{p}_N}{\mu M}\\
&\dot{\mathbf{R}}' = \tfrac{m_e\dot{\mathbf{r}}'_e + m_N\dot{\mathbf{r}}_N}{M} = \tfrac{\mathbf{p}'_e + \mathbf{p}_N}{M}
\end{aligned} \tag{15}$$

where $\mathbf{p}_N$ is the momentum of the nucleus and $\mathbf{p}_e$ is the momentum of the electron, $\mu = (m_e^{-1} + m_N^{-1})^{-1}$ and $M = m_e + m_N$. Consequently, the Schrödinger's equation becomes [86]:

$$\begin{aligned}
&-\tfrac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\vartheta(\mathbf{R}') = E_{CM}\vartheta(\mathbf{R}')\\
&\left(-\tfrac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}'} + V(\mathbf{r}')\right)\phi(\mathbf{r}') = E_\mu\phi(\mathbf{r}')
\end{aligned} \tag{16}$$

When the photon is emitted, following the same approach, we can obtain [86]:

$$\begin{aligned}
&-\tfrac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\vartheta(\mathbf{R}') = E_{CM}\vartheta(\mathbf{R}')\\
&\left(-\tfrac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right)\phi(\mathbf{r}) = E_\mu\phi(\mathbf{r})
\end{aligned} \tag{17}$$

with the wave function given as $\psi(\mathbf{r},\mathbf{R}') = \phi(\mathbf{r})\vartheta(\mathbf{R}')$. We can evaluate the energy footprint of the process as:

$$E_{ftp} = \Delta(h\nu) = \Delta E_{CM} = \langle\psi(\mathbf{r},\mathbf{R})|H|\psi(\mathbf{r},\mathbf{R}')\rangle = \frac{m_e}{M}\,h\nu \tag{18}$$

where H is the Hamiltonian of the interaction. In this way, we have proven that a microscopic irreversibility exists. Indeed, the relation (18) represents the correction term $h\nu/2Mc^2$ related to the irreversibility occurs during the photon absorption-emission process by the electron of a Hydrogen-like atom. This term can be evaluated considering that the energy of an electronic transition is of the order of 10^{-13} J, while the energy, Mc^2, related to the mass of an atom M is of the order of 10^{-8} J. So, the correction term $h\nu/2Mc^2$ is of the order of 10^{-5}–10^{-4} J, negligible compared to 1 in the denominator, obtaining the well known relation (10) used in atomic spectroscopy. But, we must highlight that for a single atom we may not consider this correction because it is very small in relation to the transition energy, but we stress that this energy correction exists, and it is the energy footprint of the process. These results allow us to explain the Carnot's results. Indeed, as a consequence of the continuous interaction between electromagnetic waves and matter, any system loses energy for microscopic irreversibility and, consequently, any system cannot convert the whole energy absorbed into work. Indeed, our result consists in pointing out that the interaction between a photon and an electron in an atom affects the energy level both of the electron and of the center of mass of the atom. When we consider a macroscopic system, we must consider the global effect of an Avogadro's number of atoms ($\sim 10^{23}$ atoms), and the macroscopic effect of the atomic energy footprint for electromagnetic interaction between atoms/molecules and photons results of the order of 10^{19}–10^{20} J mol^{-1}. This energy is lost by matter for thermal disequilibrium, which causes a continuum electromagnetic interaction [72,74,75]. But, this macroscopic irreversibility is no more than a consequence of the microscopic irreversibility. Now, we must consider the macroscopic effect of this microscopic considerations.

3. Irreversible thermodynamics analysis

Entropy may be defined as the thermal energy which cannot be turned into useful work or, sometimes, as the "disorder" in the molecular structure. Entropy is a state function and its change for a reversible system results:

$$\begin{aligned}
\Delta S_t &= \int \left(\tfrac{\delta Q}{T}\right)_{rev} = \Delta S_e + \int_0^\tau \dot{S}_g dt\\
&= \Delta S_e + \int_0^\tau \left(\tfrac{dS}{dt} - \sum_{i=1}^{n}\tfrac{\dot{Q}_i}{T_i} - \sum_{in} G_{in}s_{in} + \sum_{out} G_{out}s_{out}\right) dt
\end{aligned} \tag{19}$$

where ΔS_e is the entropy variation that could be obtained through a reversible path on which the system exchanges the same fluxes across its boundaries, $\dot{S}_g$ is the entropy generation rate, i.e. the time entropy variation due to irreversibility [77,97], τ is the lifetime of the process under consideration, which can be defined as the range of time in which the process occurs [9,77,98], and Q is the heat exchanged, T is the temperature of the thermal source, s is the specific entropy and G is the mass flow.

Entropy generation and obtained work from a system are two thermodynamic quantities related one another, because, reversible work is the maximum work that can be provided to any system, while entropy generation allows us to evaluate irreversibility, that causes a decrease of the reversible work. Work balance of the considered system can be evaluated by using the kinetic energy theorem as [70,99,100]:

$$W_{es} + W_{fe} + W_i = \Delta E_k \tag{20}$$

where W_{es} is the work done by the environment on the system, i.e. the work done by the external forces to the border of the system, W_{fe} is the work lost due to external irreversibility, E_k is the kinetic energy of the system, W_i is the internal work, such that [70]:

$$W_i = W_i^{rev} - W_{fi} \tag{21}$$

where W_i^{rev} reversible internal work and W_{fi} lost work resulted from internal irreversibility. W_{se} is the work done by the system on the environment and it can be described as [70,99,100]:

$$W_{se} = -W_{es} - W_{fe} \tag{22}$$

Consequently, it is possible to obtained the first principle of thermodynamics in different analytical expression [99,100]:

$$\begin{aligned} Q - W_{se} &= \Delta U + \Delta E_k \\ Q - W_i &= \Delta U \end{aligned} \tag{23}$$

where U the internal energy of the system. The kinetic energy variation ΔE_k can be written as follows [74]:

$$\int_0^\tau E_k\, dt = \int_0^\tau (Q - W_{se} - \Delta U)\, dt = (Q - W_{se} - \Delta U)\, \tau \tag{24}$$

According to Annila and Salthe, the Noether approach holds [101]:

$$2\int_0^\tau E_k dt = nh \quad \text{with} n \quad n \geqslant 1 \tag{25}$$

where n multiplies of quanta h is Planck constant. Using Eqs. (24) and (25), we can obtain [74]:

$$(Q - W_{se} - \Delta U)\, \tau = n\frac{h}{2} = n\pi\hbar \tag{26}$$

where $\hbar$ is reduced Planck constant, named Dirac constant. The Eq. (26) shows the relationship of the Annila and Salthe results in irreversible thermodynamics. According to Gouy-Stodola theorem, total lost work results [10–14]:

$$W^{irrev} = W_{fi} - W_{fe} = T_0 S_g \tag{27}$$

where T_0 is the environmental temperature and S_g is the entropy generation. Manipulating previous equations, we can obtain [74]:

$$(W_i^{rev} - W_{es})\, \tau = n\pi\hbar + T_0\, \tau\, S_g \tag{28}$$

Now, considering an ideal system (without irreversibilities) it follows [74]:

$$W_i^{rev} - W_{es} = \frac{n\pi\hbar}{\tau} \tag{29}$$

If the electronic transition in an atom is considered, the difference of the energy Δ in a cycle, i.e. the absorption and emission of a photon, results:

$$\Delta = (W_i^{rev} - W_{se}) + (-W_i^{rev} + W_{se}) - \frac{n\pi\hbar}{\tau} + \frac{n\pi\hbar}{\tau} \tag{30}$$

For an irreversible process the Eq. (30) becomes:

$$\Delta = (W_i^{rev} - W_{es}) + (-W_i^{rev} + W_{es}) + T_0 S_g + T_0 S_g - \frac{n\pi\hbar}{\tau} + \frac{n\pi\hbar}{\tau} = 2T_0 S_g \tag{31}$$

An atom, with ground stationary state energy E_0, which absorbs a photon of frequency ν and makes an energy state transition to an energy stationary state E_1 such that:

$$E_1 = E_0 + h\nu \tag{32}$$

Theoretically the atom can present a reverse transition to its ground state

$$E_0 = E_1 - h\nu \tag{33}$$

without any footprint Δ of the process; indeed, considering the cycle of absorption and emission of the photon the footprint results:

$$\Delta = E_1 - E_0 - E_1 + E_0 + h\nu - h\nu = 0 \tag{34}$$

But, in an atom, a bound electron interacts (electrostatic force) with the atomic nucleus and this interaction must have a consequence in the process considered, as we have highlighted in the previous section. When a photon is absorbed by a bound electron, the following transition occurs:

$$E_1 - E_0 = h\nu + E_{ka} \tag{35}$$

where E_{ka} is the kinetic energy acquired by the atom as a consequence of the energy and momentum conservation. Consequently, it is necessary a greater quantity of energy, respect to the ideal case, to obtain the same transition between the two stationary states. Then, when the photon is emitted the following transition occurs:

$$E_0 - E_1 = -h\nu + E\prime_{ka} \tag{36}$$

where E'_{ka} is the kinetic energy in the final state. The footprint of the process can be evaluated as:

$$\Delta = E_1 - E_0 - E_1 + E_0 + h\nu - h\nu + E_{ka} + E\prime_{ka} = E_{ka} + E\prime_{ka} \tag{37}$$

and, considering the relation (31) [73]:

$$S_g = \frac{E_{ka} + E\prime_{ka}}{2T_0} \tag{38}$$

where T_0 is the environmental temperature. In this case the environmental energy can be related to an energy reference state, for example the temperature of the atomic nucleus. The result obtained agrees with the previous obtained by using a quantum approach. Now, we show an example on a molecular heat engine, in order to confirm numerically our results.

4. Application to molecular heat engine

A heat engine is a cyclic engines which converts heat into work. The first law of thermodynamicsstates that the difference between the inlet and outlet energy into and out of the system is equal to internal energy change inside the system:

$$\delta Q - \delta W = dU \tag{39}$$

For a cyclic system at the steady state conditions the Eq. (39) holds:

$$\delta Q = \delta W \tag{40}$$

For a quantum thermodynamic system, heat and work changes result [60]:

$$\delta Q = \omega dS \tag{41}$$

$$\delta W = Sd\omega \tag{42}$$

where ω is the energy-level gap and S is the spin. Expectation value of spin operator is [60]:

$$S = -\frac{1}{2} Tanh\left(\frac{\beta\omega}{2}\right) \tag{43}$$

where β is the temperature (throughout this paper "temperature" will refer top rather than T for simplicity), if not stated otherwise ($\beta = l/k_B T$, where T is the absolute temperature) [60]. In the calculations, k_B and h are assumed as 1 for simplicity.

Any real engine, operating with thermodynamic cycle, always includes irreversibility, evaluated by using the entropy generation and related to the lost work consequent to irreversibility. The lost work can be obtained by comparing the heat engine operating on a

reversible (internal and external) cycle, called Carnot engine, with the real cycle. Another reference theoretical cycle is called Curzon-Ahlborn engine. It is internal reversible (endoreversible) and external irreversible. External irreversibility can be obtained by removing the work produced by endoreversible cycle from the work produced by reversible cycle. Reversible (Carnot) cycle, endoreversible and irreversible (actual heat engine) cycles for a quantum heat engine are shown in Fig. 1. Using the heat transfer equations [58], the work output of the reversible cycle of spin system can be written as follows:

$$Q_H^{rev} = \frac{\omega_1}{2} Tanh\frac{\beta_H\omega_1}{2} - \frac{\omega_2}{2} Tanh\frac{\beta_H\omega_2}{2} + \frac{1}{\beta_H}\ln\left(\frac{Cosh\frac{\beta_H\omega_2}{2}}{Cosh\frac{\beta_H\omega_1}{2}}\right) \quad (44)$$

$$Q_L^{rev} = \frac{\omega_4}{2} Tanh\frac{\beta_L\omega_4}{2} - \frac{\omega_3}{2} Tanh\frac{\beta_L\omega_3}{2} - \frac{1}{\beta_L}\ln\left(\frac{Cosh\frac{\beta_L\omega_4}{2}}{Cosh\frac{\beta_L\omega_3}{2}}\right) \quad (45)$$

$$W^{rev} = Q_H^{rev} - Q_L^{rev} \quad (46)$$

Similar to reversible cycle, the work generated by endoreversible cycle can be obtained as follows:

$$Q_H^{endo} = \frac{\omega_1'}{2} Tanh\frac{\beta_h\omega_1'}{2} - \frac{\omega_2'}{2} Tanh\frac{\beta_h\omega_2'}{2} + \frac{1}{\beta_h}\ln\left(\frac{Cosh\frac{\beta_h\omega_2'}{2}}{Cosh\frac{\beta_h\omega_1'}{2}}\right) \quad (47)$$

$$Q_L^{endo} = \frac{\omega_4'}{2} Tanh\frac{\beta_l\omega_1'}{2} - \frac{\omega_3'}{2} Tanh\frac{\beta_l\omega_2'}{2} - \frac{1}{\beta_l}\ln\left(\frac{Cosh\frac{\beta_l\omega_4'}{2}}{Cosh\frac{\beta_l\omega_3'}{2}}\right) \quad (48)$$

$$W^{endo} = Q_H^{endo} - Q_L^{endo} \quad (49)$$

where $\omega_1', \omega_2', \omega_3', \omega_4'$ are defined in the following relation [60]:

$$\omega_1' = \frac{-2Tanh^{-1}(2S_1)}{\beta_h},\quad \omega_2' = \frac{-2Tanh^{-1}(2S_2)}{\beta_h},$$
$$\omega_3' = \frac{-2Tanh^{-1}(2S_2)}{\beta_l},\quad \omega_4' = \frac{-2Tanh^{-1}(2S_1)}{\beta_l} \quad (35)$$

Here, we investigate a two-level system. The working medium is a non-interacting spin -1/2 system. We consider a heat engine cycle which involves two isothermal branches connected by two irreversible adiabatic branches. It operates between two heat reservoirs at temperature β_H and β_L, which are thermal phonon systems. The reservoirs are infinitely large and their internal relaxations are very strong. In addition, time dependent external magnetic field is applied to the system. The actual (irreversible) work (output) can be calculated by using the following equations:

$$Q_H^{irrev} = \frac{\omega_1'}{2} Tanh\frac{\beta_h\omega_1'}{2} - \frac{\omega_2'}{2} Tanh\frac{\beta_h\omega_2'}{2} + \frac{1}{\beta_h}\ln\left(\frac{Cosh\frac{\beta_h\omega_2'}{2}}{Cosh\frac{\beta_h\omega_1'}{2}}\right) \quad (50)$$

$$Q_L^{irrev} = \frac{\omega_4^*}{2} Tanh\frac{\beta_l\omega_4^*}{2} - \frac{\omega_3^*}{2} Tanh\frac{\beta_l\omega_3^*}{2} - \frac{1}{\beta_l}\ln\left(\frac{Cosh\frac{\beta_l\omega_4^*}{2}}{Cosh\frac{\beta_l\omega_3^*}{2}}\right) \quad (51)$$

$$W^{irrev} = Q_H^{irrev} - Q_L^{irrev} \quad (52)$$

According to the quantum adiabatic theorem, rapid change in the external magnetic field causes a quantum non-adiabatic phenomenon. The effect of the quantum non-adiabatic phenomenon on the performance characteristics of the heat engine cycle is similar to internally dissipative friction in the classical analysis. We use x for a parameter resulting from the internal irreversibility in adiabatic branch 2-3 and 4-1. The changes S_2 to S_3 and S_4 to S_1 are linear, so x is a first grade parameter. According to this definition, S_3 and S_4 can be written as follows [58,59]:

$$S_2 = S_3 - x \quad (53)$$

$$-\frac{1}{2}Tanh\left(\frac{\beta_H\omega_2}{2}\right) = -\frac{1}{2}Tanh\left(\frac{\beta_h\omega_3^*}{2}\right) - x \quad (54)$$

$$S_4 = S_1 - x \quad (55)$$

$$-\frac{1}{2}Tanh\left(\frac{\beta_L\omega_1}{2}\right) - x = -\frac{1}{2}Tanh\left(\frac{\beta_l\omega_4^*}{2}\right) \quad (56)$$

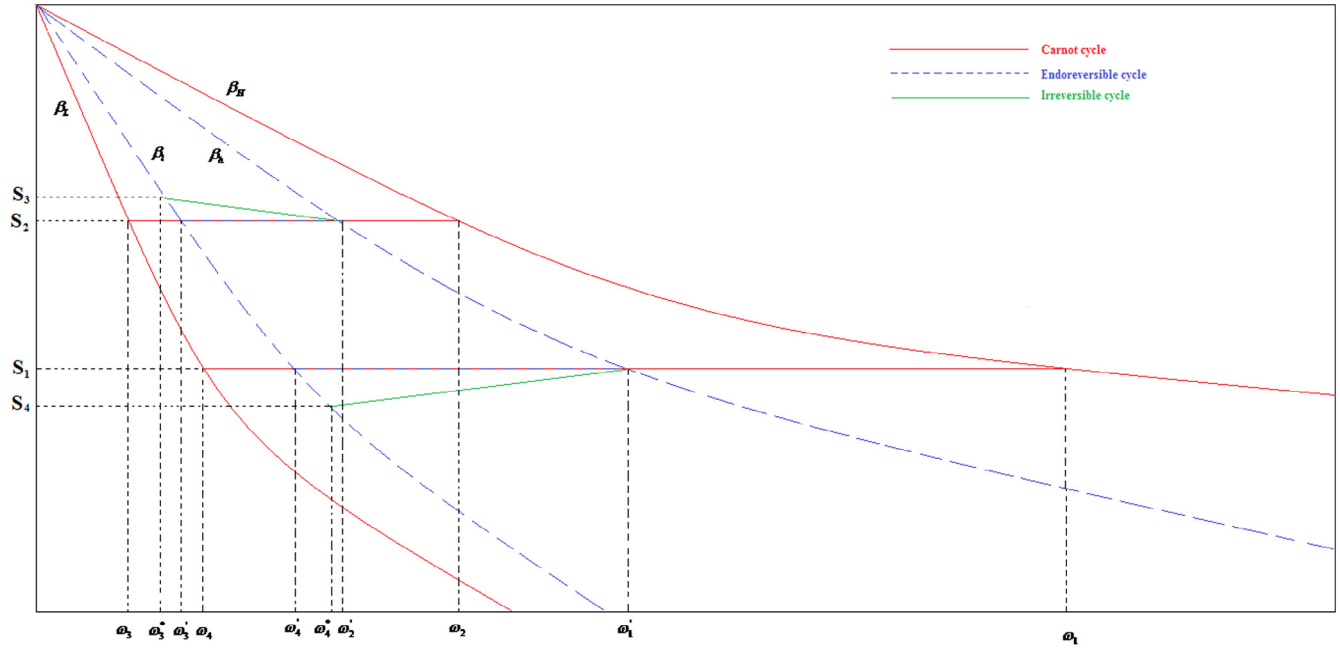

Fig. 1. Carnot quantum heat engine, endoreversible quantum heat engine and irreversible quantum heat engine. The reversible cycle, endoreversible and irreversible cycles for a quantum heat engine are represented as a two-level system with working medium as a non-interacting spin -1/2 system. We consider a heat engine cycle which involves two isothermal branches connected by two irreversible adiabatic branches. It operates between two heat reservoirs at temperature β_H and β_L, which are thermal phonon systems.

The lost work due to external irreversibility results:

$$W^{ext} = W^{rev} - W^{end} \tag{57}$$

while the lost work due to external and internal irreversibility (total irreversibility) can be obtained by removing work output of the actual heat engine from the work output obtained in the reversible heat engine:

$$W^{tot} = W^{rev} - W^{irrev} \tag{58}$$

Finally, internal irreversibility can be evaluated by as follows:

$$W^{\text{int}} = W^{tot} - W^{ext} \tag{59}$$

According to Reference [75] entropy generation can be expressed as:

$$\frac{W^{tot}}{T_o} = \frac{E_{ka} + E'_{ka}}{2T_o} \tag{60}$$

$$W^{tot} = \frac{E_{ka} + E'_{ka}}{2} \tag{61}$$

where, E_{ka} is the kinetic energy acquired by the atom as a consequence of the energy and momentum conservations and E'_{ka} is the kinetic energy of the atom in the final state, corresponding to the initial ground state of the electron involved in the transition.

External, internal and total irreversibility results:

The parameters used in calculations are listed in Table 1, while the work obtained for reversible (W^{rev}), endoreversible (W^{endo}) and irreversible cycles (W^{irrev}) are shown in Table 2. The results obtained for the quantum heat engine are matching with results of a macro scale heat engine; reversible engine developed the higher value of work, followed by the endoreversible engine and, last, by the irreversible one. This proves that the results obtained in quantum thermodynamics and in classical thermodynamics are in accordance. By using the work obtained for reversible, endoreversible and irreversible cycles, the total, external and internal irreversibility can be determined. We obtained that external irreversibility of the quantum cycle are greater (more than three times) than the internal irreversibility. We can state that irreversibility related to the finite temperature heat transfer is more effective than the irreversibility of quantum friction. In addition to that, we define total irreversibility in terms of kinetic energies as described in [74], which is just the footprint of the process considered.

5. Conclusions

The Carnot engine is a totally reversible and its efficiency represents upper limits for the efficiency of any heat engine. This means that it has maximum efficiency and maximum useful work. However, the Carnot heat engine is only a theoretical model of engine, impossible to realize. Indeed, there are always losses in actual thermal cycles, and they can be evaluated by using the entropy generation. These losses, which cause the decrease of useful work and

$$W^{ext} = \frac{1}{2\beta_h\beta_H\beta_l\beta_L}\left(\begin{array}{l} -2\beta_H\beta_l\beta_L \ln\left(\frac{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_1)}}}{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_2)}}}\right) - 2\beta_h\beta_H\beta_L \ln\left(\frac{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_2)}}}{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_1)}}}\right) + 2\beta_h\beta_l\beta_L \ln\left(\frac{Cosh(\beta_H\omega_2)}{Cosh(\beta_H\omega_1)}\right) \\ +2\beta_h\beta_H\beta_l \ln\left(\frac{Cosh\left(\frac{\beta_H\beta_l\omega_1}{2\beta_L}\right)}{Cosh\left(\frac{\beta_H\beta_l\omega_2}{2\beta_L}\right)}\right) + \beta_h\beta_H\beta_l\beta_L\omega_1 Tanh\left(\frac{\beta_H\omega_1}{2}\right) + 2\beta_H(\beta_h-\beta_l)\beta_L Arctanh\left(Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_1}{2}\right) \\ -\beta_h\beta_H^2\beta_l\omega_1 Tanh\left(\frac{\beta_H\beta_l\omega_1}{2\beta_L}\right) - \beta_h\beta_H\beta_l\beta_L\omega_2 Tanh\left(\frac{\beta_H\omega_2}{2}\right) - 2\beta_H(\beta_h-\beta_l)\beta_L Arctanh\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_2}{2}\right) \\ +\beta_h\beta_H^2\beta_l\omega_2 Tanh\left(\frac{\beta_H\beta_l\omega_2}{2\beta_L}\right) \end{array}\right) \tag{62}$$

$$W^{\text{int}} = \frac{1}{\beta_l}\left(\begin{array}{l} \ln\left(\frac{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_2)}}}{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_1)}}}\right) - \ln\left(\frac{\sqrt{1-\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)-2x\right)^2}}{\sqrt{1-\left(Tanh\left(\frac{\beta_H\omega_1}{2}\right)+2x\right)^2}}\right) - Arctanh\left(Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_1}{2}\right) \\ +ArcTanh\left(2x+Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)\left(2x+Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right) + ArcTanh\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_2}{2}\right) \\ +ArcTanh\left(2x-Tanh\left(\frac{\beta_H\omega_2}{2}\right)\right)\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)-2x\right) \end{array}\right) \tag{63}$$

$$W^{tot} = \frac{1}{2}\left(\begin{array}{l} \frac{2\ln\left(\frac{Cosh\left(\frac{\beta_H\omega_2}{2}\right)}{Cosh\left(\frac{\beta_H\omega_1}{2}\right)}\right)}{\beta_H} - \frac{2\ln\left(\frac{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_1)}}}{\sqrt{\frac{1}{1+Cosh(\beta_H\omega_2)}}}\right)}{\beta_h} + \frac{2\ln\left(\frac{Cosh\left(\frac{\beta_H\beta_l\omega_1}{2\beta_L}\right)}{Cosh\left(\frac{\beta_H\beta_l\omega_2}{2\beta_L}\right)}\right)}{\beta_L} - \frac{2\ln\left(\frac{\sqrt{1-\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)-2x\right)^2}}{\sqrt{1-\left(Tanh\left(\frac{\beta_H\omega_1}{2}\right)+2x\right)^2}}\right)}{\beta_l} \\ +\omega_1 Tanh\left(\frac{\beta_H\omega_1}{2}\right) - \frac{2Arctanh\left(Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_1}{2}\right)}{\beta_h} + \frac{2Arctanh\left(2x+Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)\left(2x+Tanh\left(\frac{\beta_H\omega_1}{2}\right)\right)}{\beta_l} \\ -\frac{\beta_H\omega_1 Tanh\left(\frac{\beta_H\beta_l\omega_1}{2\beta_L}\right)}{\beta_L} - \omega_2 Tanh\left(\frac{\beta_H\omega_2}{2}\right) + \frac{2Arctanh\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)\right)Tanh\left(\frac{\beta_H\omega_2}{2}\right)}{\beta_h} \\ +\frac{2Arctanh\left(2x-Tanh\left(\frac{\beta_H\omega_2}{2}\right)\right)\left(Tanh\left(\frac{\beta_H\omega_2}{2}\right)-2x\right)}{\beta_l} + \frac{\beta_H\omega_2 Tanh\left(\frac{\beta_H\beta_l\omega_2}{2\beta_L}\right)}{\beta_L} \end{array}\right) \tag{64}$$

Table 1
Parameters used in calculations.

Parameter	Unit	Value
β_H	J^{-1}	0.0100
β_L	J^{-1}	0.0333
β_h	J^{-1}	0.0111
β_l	J^{-1}	0.0313
x	–	0.0003
ω_1	J	5
ω_2	J	3

Table 2
Calculated values for the cycle.

Parameter	Unit	Value
W^{rev}	J	0.0141
W^{endo}	J	0.0116
W^{irrev}	J	0.0108
W^{ext}	J	0.0025
W^{int}	J	0.0008
W^{tot}	J	0.0033

the engine efficiency, are called lost work, or exergy destruction. The causes of the irreversibility may be classified in internal and external. So, the Carnot heat engine is totally reversible, there is no irreversibility or lost work in it, while the endoreversible heat engine is internally reversible but, externally irreversible. In classical thermodynamics, relationship between these heat engines can be defined and the irreversibility might be evaluated.

Here, the lost works are determined for a molecular heat engine, that is a -1/2 spin system. It follows that results correspond to a macro heat engines. In addition, our results agree with the ones obtained in Refs. [97–101], related to micro/molecular heat engines and quantum thermodynamics. These results are fundamental in relation to nano/quantum thermodynamics because of their advances in nano-technology.

The relations obtained show that during any process, there always exist the irreversibility, due to interaction of the electromagnetic waves, present in the environment, with the matter, even if mechanical frictions don't exist. This irreversibility is related to the nature itself of the matter, and it is due to the existence of the spontaneous flows between open systems and environment due to thermal disequilibrium. Consequently, part of the energy absorbed by the system is converted into atomic irreversibility and cannot be used to convert the absorbed heat into work. Here, we have suggested a new approach to explain the macroscopic irreversibility in thermodynamics by introducing an energy footprint in quantum mechanics and deriving a change in the Schrödinger's equation for a Hydrogen-like atom. We have followed the Einstein's, Schrödinger's and Gibbs considerations on the interaction between particles and thermal radiation (photons), which leads to consider the atom as an open system in interaction with an external flows of photons. In conclusion, we state that the quantum mechanical analysis shows that particle path information isn't preserved because the particle interactions with photons in the thermal radiation field change the internal states of the particles themselves with a microscopically irreversibility, in accordance with the irreversible measurements that John von Neumann showed increase the entropy [102]. The results here obtained is a confirmation of the hypothesis that an energy footprint due to irreversibility exists also in atomic level transition [72,74,75,103,104]. Irreversibility is the result of the interaction between open system and its environment. Our results link one another the different approaches to irreversibility in thermodynamics (macro-approach [105–119], micro/nano-approach [120–125], adn quantum approach [126,127]) with particular interest in the analysis of molecular engines.

Last, in 1889, Gouy proved that the exergy lost in a process is proportional to the entropy generation. Consequently, the exergy flows, which means the flows of free energy, entail any process where the system evolves from one state to another. The free energy is the base of any evolutionary process, so that quanta are either absorbed from the surroundings to the system's in the form bound energy or emitted from the system to its surroundings. It occurs in the least time. During this interaction the systems exchange quanta, thermodynamically evaluated by exergy flows with consequent entropy generation due to irreversibility. So, it is the exergy flow between system and environment which renders the evolution irreversible: these flows of energy 'select and shape' the paths 'delivering least time energy dispersal'. These considerations open a new viewpoint to quantum systems, which could be studied by the recent theory of Constructal law, bringing in a near future, to the quantum constructal law.

Author contributions

U.L. developed the quantum thermodynamic approach. E.A. developed the molecular heat engine application.

References

[1] I. Dincer, Y.A. Cengel, Energy, entropy and exergy concepts and their roles in thermal engineering, Entropy 3 (2001) 116–149.
[2] S. Dolev, A.C. Elitzur, Biology and thermodynamics: seemingly-opposite phenomena in search of a unified paradigm, Einstein Q.: J. Biol. Med. 15 (1998) 24–33.
[3] S. Carnot, Rèflexion sur la puissance motrice du feu sur le machine a dèvelopper cette puissance, Bachelier Libraire, Paris, 1824.
[4] U. Lucia, Carnot efficiency: Why?, Physica A 392 (2013) 3513–3517
[5] R. Clausius, Mechanical Theory of Heat – with its Applications to the Steam Engine and to Physical Properties of Bodies, John van Voorst, London, 1865.
[6] B.H. Lavenda, Thermodynamics of Irreversible Processes, Dover, Mineola, USA, 1993.
[7] C. Truesdell, Rational Thermodynamics, Springer-Verlag, Berlin, Germany, 1984.
[8] A. Bejan, Shape and Structure, from Engineering to Nature, Cambridge University Press, Cambridge, 2010.
[9] U. Lucia, Stationary open systems: a brief review on contemporary theories on irreversibility, Physica A 392 (2013) 1051–1062.
[10] G. Gouy, Sur les transformation et l'équilibre en Thermodynamique, Comptes Rendus de l'Acadèmie des Sciences Paris 108 (1889) 507–509.
[11] G. Gouy, Sur l'énergie utilizable, Journal de Physique 8 (1889) 501–518.
[12] P. Duhem, Sur les transformations et l'équilibre en Thermodynamique, Note de M.P. Duhem, Comptes Rendus de l'Acadèmie des Sciences Paris 108 (1889) 666–667.
[13] G. Gouy, Sur l'énergie utilisable et le potentiel thermodynamique, Note de M. Gouy, Comptes Rendus de l'Acadèmie des Sciences Paris 108 (1889) 794.
[14] A. Stodola, (translated by L.C. Loewenstein), Steam Turbine; Van Nostrand, New York, 1905.
[15] I. Prigogine, Modération et transformations irréversibles des systèmes ouverts, Bulletin de la Classe des Sciences, Académie Royale de Belgique 31 (1945) 600–606.
[16] I. Prigogine, Étude thermodynamique des Phenomènes Irréversibles, Desoer, Liège, Belgium, 1947.
[17] I. Prigogine, Introduction to Thermodynamics of Irreversible Processes, Thomas Springfields, 1955.
[18] I. Prigogine, Structure, Dissipation and Life, in: M. Marois (Ed.), Theoretical Physics and Biology, North Holland Pub. Co., Amsterdam, The Netherlands, 1969, pp. 23–52.
[19] P. Glansdorff, I. Prigogine, Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley-Interscience, New York, 1971.
[20] G. Nicolis, Stability and dissipative structures in open systems far from equilibrium, in: I. Progogine, S.A. Rice (Eds.), Advances in Chemical Physics, Wiley-Interscience, New York, 1971, pp. 209–324.
[21] D. Kondepudi, I. Prigogine, Modern Thermodynamics, From Heat Engine to Dissipative Structures, Wiley, New York, 1999.
[22] I. Prigogine, Time, structure, and fluctuations, Science 201 (4358) (2001) 777–785.
[23] H. Ziegler, Thermodynamik und rheologische Probleme, Ing. Arch. 25 (1957) 58–70.
[24] H. Ziegler, Chemical reactions and the principle of maximal rate of entropy production, Appl. Math. Phys. ZAMP 34 (1928) 832–844.

[25] H. Ziegler, Introduction to Thermomechanics, North-Holland, Amsterdam, 1983.
[26] H. Ziegler, C. Wehrli, On a principle of maximal rate of entropy production, J. Non-Equilib. Thermodyn. 12 (1987) 229–243.
[27] F. Wu, L. Chen, F. Sun, C. Wu, F. Guo, Q. Li, Quantum degeneracy effect on performance of irreversible Otto cycle with ideal Bose gas, Energy Convers. Manage. 47 (2006) 3008–3018.
[28] J. He, H. Wang, S. Liu, Performance characteristics of a quantum Diesel refrigeration cycle, Energy Convers. Manage. 50 (2009) 933–937.
[29] H. Saygın, A. Şişman, Brayton refrigeration cycles working under quantum degeneracy, Appl. Energy 69 (2001) 77–85.
[30] B. Lin, Y. Zhang, J. Chen, Influence of quantum degeneracy and regeneration on the performance of Bose-Stirling refrigeration cycles operated in different temperature regions, Appl. Energy 83 (2006) 513–535.
[31] W. Nie, Q. Liao, C.Q. Zhang, J. He, Micro-/nanoscaled irreversible Otto engine cycle with friction loss and boundary effects and its performance characteristics, Energy 35 (2010) 4658–4662.
[32] J. Guo, X. Zhang, G. Su, J. Chen, The performance analysis of a micro-/nanoscaled quantum heat engine, Physica A 391 (2012) 6432–6439.
[33] E. Açıkkalp, N. Caner, Determining performance of an irreversible nano scale dual cycle operating with Maxwell-Boltzmann gas, Physica A 424 (2015) 342–349.
[34] F. Wu, L. Chen, S. Wu, Ecological Optimization Performance of an Irreversible Quantum Otto Cycle Working with an Ideal Fermi Gas, Open System and Information Dynamics 13 (2006) 55–66.
[35] E. Açıkkalp, N. Caner, Determining of the optimum performance of a nano scale irreversible Dual cycle with quantum gases as working fluid by using different methods, Physica A 433 (2015) 247–258.
[36] E. Açıkkalp, N. Caner, Performance of an irreversible nano Brayton cycle operating with Maxwell- Boltzmann Gas, European Physical Journal Plus 130 (2015) 93.
[37] H. Wang, S. Liu, J. He, Optimum criteria of an irreversible quantum Brayton refrigeration cycle with an ideal Bose gas, Physica B 403 (2008) 3867–3878.
[38] J. Liu, B. Lin, W. Hu, J. Chen, Influence of multi-irreversibilities on the performance of a Brayton refrigeration cycle working with an ideal Bose or Fermi gas, Int. J. Therm. Sci. 47 (2008) 1374–1381.
[39] H. Wang, S. Liu, J. He, Performance analysis and parametric optimum criteria of a quantum Otto heat engine with heat transfer effects, Appl. Therm. Eng. 29 (2009) 706–711.
[40] A. Şişman, H. Saygin, On the power cycles working with ideal quantum gases: I. The Ericsson cycle, J. Phys. D: Appl. Phys. 32 (1999) 664–670.
[41] J. Chen, J. He, B. Hua, The influence of regenerative losses on the performance of a Fermi Ericsson refrigeration cycle, J. Phys. A: Math. Gen. 35 (2002) 7995–8004.
[42] Y. Zhang, B. Lin, J. Chen, The influence of quantum degeneracy and irreversibility on the performance of a Fermi quantum refrigeration cycle, J. Phys. A: Math. Gen. 37 (2004) 7485–7497.
[43] A. Şişman, H. Saygin, Efficiency Analysis of a Stirling Power cycle Under quantum degeneracy conditions, Physica Scripta 63 (2001) 263–267.
[44] A. Şişman, H. Saygin, Re-optimization of Otto power cycles working with ideal quantum gasses, Physica Scripta 64 (2001) 108–112.
[45] H. Wang, S. Liu, J. Du, Performance analysis and parametric optimum criteria of a regeneration Bose-Otto engine, Phys. Scr. 79 (2009) 055004.
[46] W. Hao, W. Guo-Xing, Optimization criteria of a Bose Brayton heat engine, Chin. Phys. B 21 (2012) 010505.
[47] A. Şişman, H. Saygin, The improvement effect of quantum degeneracy on the work from a Carnot cycle, Appl. Energy 68 (2001) 367–376.
[48] B. Lin, J. Chen, The performance Analysis of a Quantum Brayton Refrigeration cycle with ideal Bose gas, Open Sys. Inf. Dyn. 10 (2003) 147–157.
[49] B. Lin, J. Chen, The Influence of Quantum Degeneracy on the Performance of a Fermi Brayton Engine, Open Sys. & Information Dyn. 11 (2004) 87–99.
[50] F. Wu, L. Chen, F. Sun, C. Wu, F. Guo, Optimal performance of an irreversible quantum Brayton refrigerator with ideal Bose gases, Phys. Scr. 73 (2006) 452–457.
[51] F. Wu, L. Chen, S. Wu, Optimization criteria for an irreversible quantum Brayton engine with an ideal bose gas, J. Appl. Phys. 99 (2006) 54904–54909.
[52] X. Liu, L. Chen, F. Wu, F. Sun, Optimal performance of a spin quantum Carnot heat engine with multi-irreversibilities, J. Energy Inst. 87 (2014) 69–80.
[53] L. Chen, X. Liu, Y. Ge, F. Wu, F.I. Sun, Ecological optimization of an irreversible harmonic oscillators Carnot refrigerator, J. Energy Inst. 86 (2013) 85–96.
[54] E. Açıkkalp, N. Caner, Application of exergetic sustainable index to the quantum irreversible Diesel refrigerator cycles for 1-D box system, Eur. Phys. J. Plus 130 (2015) 73.
[55] X. Liu, L. Chen, Y. Ge, F. Wu, F. Sun, Fundamental optimal relation of a spin 1/2 quantum Brayton heat engine with multi-irreversibilities, Scientia Iranica: Trans. B-Mech. Eng. 19 (2012) 1124–1132.
[56] X. Liu, L. Chen, F. Wu, F. Sun, Fundamental optimal relation of an irreversible quantum Carnot heat pump with spin-1/2 systems, Math. Comput. Model. 54 (2011) 190–202.
[57] X. Liu, L. Chen, F. Wu, F. Sun, Cooling load and energy efficiency optimization of an irreversible Carnot refrigerator with spin-1/2 systems, Int. J. Energy Environ. 2 (2011) 797–812.
[58] X. Liu, L. Chen, F. Wu, F. Sun, Ecological optimization of an irreversible quantum Carnot heat engine with spin-1/2 systems, Phys. Scr. 81 (2010) 025003.
[59] T. Feldmann, R. Kosloff, Performance of discrete heat engines and heat pumps in finite time, Phys. Rev. E 61 (2000) 4774–4790.
[60] E. Geva, R. Kosloff, A quantum-mechanical heat engine operating in finite time. a model consisting of spin-1/2 systems as working fluid, J. Chem. Phys. 96 (1992) 3054–3067.
[61] F. Wu, L.G. Chen, F.R. Sun, C. Wu, Performance of an irreversible quantum Carnot engine with spin-1/2, J. Chem. Phys. 124 (2006) 214702.
[62] F. Wu, L.G. Chen, F.R. Sun, C. Wu, Q. Li, Generalized model and optimum performance of an irreversible quantum Brayton engine with spin systems, Phys. Rev. E 7 (2006) 016103.
[63] G.P. Beretta, Quantum thermodynamic Carnot and Otto-like cycles for a two-level system, EPL 99 (2012) 20005.
[64] M.J. Henrich, F. Rempp, G. Mahler, Quantum thermodynamic Otto machines: a spin-system approach, Eur. Phys. J. Special Topics 151 (2007) 157–165.
[65] X.-L. Huang, X.-Y. Niu, X.-M. Xiu, X.-X. Yi, Quantum Stirling heat engine and refrigerator with single and coupled spin systems, Eur. Phys. J. D 68 (2014) 32.
[66] M. Azimi, L. Chotorlishvili, S.K. Mishra, T. Vekua, W. Hübner, J. Berakdar, Quantum Otto heat engine based on a multiferroic chain working substance, New J. Phys. 16 (2014) 063018.
[67] W. Hübner, G. Lefkidis, C.D. Dong, D. Chaudhuri, Spin-dependent Otto quantum heat-engine based on molecular substance, Phys. Rev. B 90 (2014) 024401.
[68] H. Wang, G. Wu, D. Chen, Thermal entangled quantum Otto engine based on the two qubits Heisenberg model with Dzyaloshinskii-Moriya interaction in an external magnetic field, Phys. Scr. 86 (2012) 015001.
[69] A. Dalkıran, E. Açıkkalp, N. Caner, Analysis of a quantum irreversible Otto cycle with exergetic sustainable index, Physica A 453 (2016) 316–326.
[70] E. Açıkkalp, N. Caner, Application of exergetic sustainability index to an nano - scale irreversible Brayton cycle operating with ideal Bose and Fermi gasses, Phys. Lett. A 379 (2015) 1990–1997.
[71] A. Dalkıran, E. Açıkkalp, A.F. Savaş, Analysis of a nano-scale thermo-acoustic refrigerator, Int. J. Refrig 66 (2016) 1–9.
[72] U. Lucia, Entropy production and generation: clarity from nanosystems considerations, Chem. Phys. Lett. 629 (2015) 87–90.
[73] U. Lucia, A Link between Nano- and Classical Thermodynamics: Dissipation Analysis, The Entropy Generation Approach in Nano-Thermodynamics, Entropy 17 (2015) 1309–1328.
[74] U. Lucia, Quanta and entropy generation, Physica A 419 (2015) 115–121.
[75] U. Lucia, Some considerations on molecular machines and Loschmidt paradox, Chem. Phys. Lett. 623 (2015) 98–100.
[76] L. Carnot, Principes fondamentaux de l'équilibre et du movement [Fundamental Principles of Equilibrium and Movement], Paris, 1803.
[77] A. Bejan, Advanced Engineering Thermodynamics, John Wiley, NJ, 2006.
[78] A. Durmayaz, O.S. Sogut, B. Sahin, H. Yavuz, Optimization of thermal systems based on finite-time thermodynamics and thermoeconomics, Prog. Energy Combust. Sci. 30 (2004) 175–217.
[79] F.L. Curzon, B. Ahlborn, Efficiency of a Carnot engine at maximum power output, Am. J. Phys. 43 (1975) 22–24.
[80] A. Bejan, Entropy Generation through Heat and Fluid Flow, Wiley, New York, 1982.
[81] A. Bejan, Entropy generation minimization, CRC Press, Boca Raton, FL, 1996.
[82] A. Bejan, G. Tsatsaronis, M. Moran, Thermal Design and Optimization, Wiley, New York, 1996.
[83] M.H. Ahmadi, M.A. Ahmadi, F. Pourfayaz, Thermodynamic analysis and evolutionary algorithm based on multi-objective optimization performance of actual power generating thermal cycles, Appl. Therm. Eng. 99 (2016) 996–1005.
[84] C. Wu, L. Chen, J. Chen (Eds.), Recent advances in finite time thermodynamics, Nova Science Publishers, New York, 1999.
[85] R.S. Berry, V. Kazakov, S. Sieniutycz, Z. Szwast, A.M. Tsirlin, Thermodynamic optimization of finite-time processes, Wiley, New York, 2000.
[86] U. Lucia, Macroscopic irreversibility and microscopic paradox: A Constructal law analysis of atoms as open systems, Sci. Rep. 6 (2016) 35796.
[87] R.O. Doyle, The continuous spectrum of the hydrogen quasi-molecule, J. Quant. Spectrosc. Radiat. Transfer 8 (1968) 1555–1569.
[88] M. Alonso, E. Finn, Quantum and Statistical Physics, Addison-Wesley, Reading, 1968.
[89] J.C. Slater, Theory of Matter, McGraw-Hill, New York, 1968.
[90] M. Planck, The Theory of Heat Radiation, Dover Publications, New York, 1991.
[91] E. Schrödinger, What's life, Cambridge University Press, Cambridge, 1944.
[92] G. Herzberg, Atomic Spectra and Atomic Structure, Dover Press, New York, 1944.
[93] W. Finkelnburg, Structure of Matter, Academic Press, New York, 1964.
[94] L.D. Landau, E.M. Lifshitz, Quantum Mechanics, Pergamon Press, Oxford, 1965.
[95] R. Feynman, R.B. Leighton, M. Sans, The Feynman Lectures on Physics, vol. III, Addison Wesley, Boston, 1964.
[96] R. Feynman, R.B. Leighton, M. Sans, The Feynman Lectures on Physics, vol. II, Addison Wesley, Boston, 1964.
[97] U. Lucia, Exergy flows as bases of constructal law, Physica A 392 (24) (2013) 6284–6287.
[98] U. Lucia, Entropy generation in technical physics, Kuwait J. Sci. Eng. 39 (2012) 91–101.
[99] U. Lucia, Molecular machine as chemical-thermodynamic devices, Chem. Phys. Lett. 556 (2013) 242–244.

[100] U. Lucia, Entropy generation: from outside to inside!, Chem Phys. Lett. 583 (2013) 209–212.
[101] A. Annila, S. Salthe, Threads of time, ISRN Thermodynamics 850957 (2012) 1–7.
[102] J. von Neumann, The Mathematical Foundations of Quantum Mechanics, Princeton University Press, Princeton, 1955.
[103] U. Lucia, Second law considerations on the third law: From Boltzmann and Loschmidt paradox to non equilibrium temperature, Physica A 444 (2016) 121–128.
[104] U. Lucia, Electron-photon interaction and thermal disequilibrium irreversibility, Int. J. Quantum Foundation 3 (2017) 24–30.
[105] B. Andresen, R.S. Berry, M.J. Ondrechen, P. Salamon, Thermodynamics for processes in finite time, Acc. Chem. Res. 17 (8) (1984) 266–271.
[106] A. Bejan, Entropy generation minimization: The new thermodynamics of finite-size devices and finite-time processes, J. Appl. Phys. 79 (3) (1996) 1191–1218.
[107] K.H. Hoffmann, J.M. Burzler, S. Schubert, Endoreversible thermodynamics, J. Non-Equilib. Thermodyn. 22 (4) (1997) 311–355.
[108] L.G. Chen, C. Wu, F.R. Sun, Finite time thermodynamic optimization or entropy generation minimization of energy systems, J. Non-Equilib. Thermodyn. 24 (4) (1999) 327–359.
[109] S. Sieniutycz, Hamilton-Jacobi-Bellman framework for optimal control in multistage energy systems, Phys. Rep. 326 (4) (2000) 165–285.
[110] L.G. Chen, F.R. Sun, Advances in Finite Time Thermodynamics: Analysis and Optimization, Nova Science Publishers, New York, 2004.
[111] L.G. Chen, Finite-Time Thermodynamic Analysis of Irreversible Processes and Cycles, Higher Education Press, Beijing, 2005.
[112] B. Andresen, Current trends in finite-time thermodynamics, Angewandte Chemie Int. Ed. 50 (12) (2011) 2690–2704.
[113] S. Sieniutycz, J. Jezowski, Energy Optimization in Process Systems and Fuel Cells, Elsevier, Oxford, 2013.
[114] L.G. Chen, F.K. Meng, F.R. Sun, Thermodynamic analyses and optimizations for thermoelectric devices: the state of the arts, Sci. China: Technol. Sci. 59 (3) (2016) 442–455.
[115] Y.L. Ge, L.G. Chen, F.R. Sun, Progress in finite time thermodynamic studies for internal combustion engine cycles, Entropy 18 (4) (2016) 139.
[116] L.G. Chen, H.J. Feng, Z.H. Xie, Generalized thermodynamic optimization for iron and steel production processes: theoretical exploration and application cases, Entropy 18 (10) (2016) 353.
[117] L.G. Chen, S.J. Xia, Generalized Thermodynamic Dynamic-Optimization for Irreversible Processes, Science Press, Beijing, 2017.
[118] L.G. Chen, S.J. Xia, Generalized Thermodynamic Dynamic-Optimization for Irreversible Cycles, Science Press, Beijing, 2017.
[119] Y.H. Bi, L.G. Chen, Finite Time Thermodynamic Optimization for Air Heat Pumps, Science Press, Beijing, 2017.
[120] Z.M. Ding, L.G. Chen, W.H. Wang, F.R. Sun, Progress in study on finite time thermodynamic performance optimization for three kinds of microscopic energy conversion systems, Scientia Sinica: Technologica 45 (9) (2015) 889–918.
[121] M.H. Ahmadi, M.A. Ahmadi, F. Pourfayaz, M. Bidi, Entransy analysis and optimization of performance of nano-scale irreversible Otto cycle operating with Maxwell-Boltzmann ideal gas, Chem. Phys. Lett. 658 (2016) 293–302.
[122] S.A. Sadatsakkak, M.H. Ahmadi, M.A. Ahmadi, Optimization performance and thermodynamic analysis of an irreversible nano scale Brayton cycle operating with Maxwell-Boltzmann gas, Energy Convers. Manage. 101 (2015) 592–605.
[123] M.H. Ahmadi, M.A. Ahmadi, A. Maleki, F. Pourfayaz, M. Bidi, E. Açıkkalp, Exergetic sustainability evaluation and multi-objective optimization of performance of an irreversible nanoscale Stirling refrigeration cycle operating with Maxwell-Boltzmann gas, Renew. Sustain. Energy Rev. 78 (2017) 80–92.
[124] M.A. Ahmadi, M.A. Nabakhteh, M.A. Ahmadi, F. Pourfayaz, M. Bidi, Investigation and optimization of performance of nano-scale Stirling refrigerator using working fluid as Maxwell-Boltzmann gases, Physica A: Stat. Mech. Appl. 483 (2017) 337–350.
[125] M.H. Ahmadi, M.A. Ahmadi, F. Pourfayaz, Performance assessment and optimization of an irreversible nano-scale Stirling engine cycle operating with Maxwell-Boltzmann gas, Eur. Phys. J. Plus 130 (9) (2015) 1–13.
[126] R. Kosloff, Quantum thermodynamics: A dynamical viewpoint, Entropy 15 (6) (2013) 2100–2128.
[127] R. Kosloff, Y. Rezek, The quantum harmonic Otto cycle, Entropy 19 (4) (2017) 136.