First-order irreversible thermodynamic approach to a simple energy converter

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Several authors have shown that dissipative thermal cycle models based on finite-time thermodynamics exhibit loop-shaped curves of power output versus efficiency, such as it occurs with actual dissipative thermal engines. Within the context of first-order irreversible thermodynamics (FOIT), in this work we show that for an energy converter consisting of two coupled fluxes it is also possible to find loop-shaped curves of both power output and the so-called ecological function versus efficiency. In a previous work Stucki [J. W. Stucki, Eur. J. Biochem. **109**, 269 (1980)] used a FOIT approach to describe the modes of thermodynamic performance of oxidative phosphorylation involved in adenosine triphosphate (ATP) synthesis within mithochondrias. In that work the author did not use the mentioned loop-shaped curves and he proposed that oxidative phosphorylation operates in a steady state at both minimum entropy production and maximum efficiency simultaneously, by means of a conductance matching condition between extreme states of zero and infinite conductances, respectively. In the present work we show that all Stucki's results about the oxidative phosphorylation energetics can be obtained without the so-called conductance matching condition. On the other hand, we also show that the minimum entropy production state implies both null power output and efficiency and therefore this state is not fulfilled by the oxidative phosphorylation performance. Our results suggest that actual efficiency values of oxidative phosphorylation performance are better described by a mode of operation consisting of the simultaneous maximization of both the so-called ecological function and the efficiency.

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I. INTRODUCTION

It is well-known that in actual dissipative heat engines, the experimental plots of power output against thermal efficiency are loop-shaped curves, where both the maximum power and maximum efficiency points do not coincide and their separation can be managed by some phenomenological parameters which depend on the engine's design and the materials employed in its construction [1,2]. In these engines it is common to find irreversibilities (losses) due to friction and irreversible heat fluxes. These losses must be taken into account in the models developed to describe engines' general performance. In the thermal engine modeling these kinds of losses are usually considered in a separate manner. However, one can couple the dissipative processes in such a way that loop-shaped curves are recovered. Several authors [2,3] have proposed thermal engine models which reproduce the loop-shaped curves observed in actual engines. This is accomplished by means of characteristic functions (as power and efficiency) depending on the thermal reservoir temperatures, and other parameters as compression ratios, and thermal conductances, for example. Through these quantities one can control the distance between the maxima points of both power output and efficiency.

In the present work (Sec. II), we show that in the case of a linear energy converter consisting of two coupled fluxes described by first-order irreversible thermodynamics (FOIT), in which one spontaneous flow manages a nonspontaneous one, loop-shaped curves (LSC) similar to those appearing in irreversible thermal engine models can also be obtained. These LSC for our FOIT model are obtained for both power output (P) versus efficiency (η) and for ecological function (E) versus η, where the ecological function is defined as the power output minus the dissipation function ($T\sigma$, see Sec. II B) [4]. In both loop-shaped curves a force ratio appears and is given by [5]

$$x = \sqrt{\frac{L_{11}}{L_{22}}}\frac{X_1}{X_2} \tag{1}$$

(where L_{ij} are the FOIT-phenomenological coefficients), which measures a direct relationship between the two forces X_1 and X_2 involved in the coupled flows. On the other hand, we also use a coupling parameter q given by

$$q = \frac{L_{12}}{\sqrt{L_{11}L_{22}}}. \tag{2}$$

This parameter gives us a measure of the coupling of spontaneous and nonspontaneous fluxes [6]. Moreover, in Sec. II we show that by means of the LSC properties it is possible to study several performance modes of the energy converter similar to those used in finite time thermodynamics (FTT) [7–10], but with further results which consist in a set of

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functions describing how the maxima points can move one with respect to the other. As an example of our previous results, we study the adenosine triphosphate (ATP) production within mitochondria by the respiration. A FOIT approach to this problem was previously published by Stucki [11]. Stucki's approach was mainly based on using two fluxes and two forces subject to several optimization criteria proposed by this author. Stucki's results regarding the economic degrees of coupling of oxidative phosphorylation arise from the assumption that mitochondria is in a steady state corresponding to minimum entropy production and that simultaneously corresponds to a maximum efficiency state. This last situation stems from the so-called conductance-matching condition (CMC), which is obtained by the inclusion of a third term in the expression for the entropy production, and corresponds to an attached cellular load under steady state conditions. This third-term phenomenological coefficient can be set to obtain the minima values of entropy production that coincide with the optimum values of efficiency. Stucki uses several objective functions to model different mitochondria operation modes, but only using the former two forces and two fluxes system and assuming the implicit holding of the conductance-matching condition. In the present paper by means of the coupling of only two fluxes and two forces some of the main Stucki results are recovered without the inclusion of the third term in entropy production corresponding to the attached cellular load. This suggests that the attached load is not necessary to describe the energetics of a linear energy converter consisting of a pair of coupled processes, where one drives the other. In summary, we show that the minimum entropy production steady state regime is not equivalent to the optimum efficiency steady state regime. This assertion arises from the fact that the Stucki results are obtained here without assuming an attached cellular load. If Stucki's third term in the entropy production is considered, then the energetics formalism should be rewritten in terms of a 3×3 matrix of phenomenological coefficients, with its consequent changes in quantities such as the efficiency and the power output. The present paper is organized as follows: In Sec. II we discuss the energetics of a 2×2 *system*; in Sec. III, we apply some of the results of the previous section on the ATP production under a linear approach. Finally in Sec. IV we present some concluding remarks.

II. ENERGETICS OF A TWO-COUPLED FLUXES SYSTEM

In this section we study the following performance regimes: the minimum dissipation function (MDF) [12], the maximum power output (MPO) [13], and the maximum ecological function (MEF) [14,15]. By means of these criteria we reproduce some previous results [11] and we obtain some different ones. In particular, we will show that a linear isothermal-isobaric engine working in the MEF regime can reach an efficiency as high as $\eta_{MEF}=0.75$.

A. Constitutive equations

Let J_1 and J_2 be two coupled generalized fluxes (J_1 being the driven flux and J_2 the driver flux); X_1 and X_2 are the conjugate generalized potentials associated with the fluxes. For the linear case, fluxes and potentials are given by the Onsager equations:

$$J_1 = \sqrt{L_{11}}(\sqrt{L_{11}}X_1 + q\sqrt{L_{22}}X_2), \tag{3}$$

$$J_2 = \sqrt{L_{22}}(q\sqrt{L_{11}}X_1 + \sqrt{L_{22}}X_2), \tag{4}$$

with $L_{12}=L_{21}$, the Onsager symmetry relation between crossed coefficients. In these equations we use the coupling coefficient defined by Eq. (2) [6]. Thus in the limit case when $q\to0$, each flux is proportional to its proper conjugate potential through its direct phenomenological coefficient, that is, the crossed effects vanish, and therefore the fluxes become independent. When $q\to1$, the fluxes tend to a mechanistic stoichiometry fixed relationship independently of the potential magnitudes [11].

On the other hand, it is convenient to define a parameter describing the cross effect between two potentials. Taking $X_2>0$ as the associated potential to the driver flux, we define the parameter x [see Eq. (1)] measuring the fraction of $X_1<0$ appearing due to the presence of the flux J_2. This parameter is a quantity with values in the interval $[-1,0]$. To complete the set of constitutive equations, we define the efficiency of the thermodynamic process as follows:

$$\eta = \frac{\text{energy output}}{\text{energy input}},$$

and following Caplan and Essig [6], in terms of Onsager relations we have

$$\eta = -\frac{TJ_1X_1}{TJ_2X_2} = -\frac{\sqrt{L_{11}}(\sqrt{L_{11}}X_1 + q\sqrt{L_{22}}X_2)X_1}{\sqrt{L_{22}}(q\sqrt{L_{11}}X_1 + \sqrt{L_{22}}X_2)X_2}. \tag{5}$$

From Eq. (1), we get the following expression for η in terms of x and q:

$$\eta(x,q) = -\frac{(x+q)x}{qx+1}. \tag{6}$$

A plot of η versus x for a fixed q is depicted in Fig. 1. This graph is a convex curve with only one maximum point. That is, there exists a relationship between the input and output energetic fluxes which maximize the efficiency for some given Onsager coefficients. We take now a linear isothermal-isobaric conversion process and build its characteristic functions in terms of q and x for determining the performance conditions correspondent to the maximization of a certain objective function. The characteristic functions we consider are the dissipation function, the power output, and the ecological function.

B. Characteristic functions

Dissipation function. Within the FOIT framework, the entropy production for a 2×2 *system* of fluxes and forces is given by [6,16],

$$\sigma = J_1X_1 + J_2X_2, \tag{7}$$

and following Tribus [5], the dissipation function for an isothermal system can be expressed as $\Phi=T\sigma$. By the substitu-

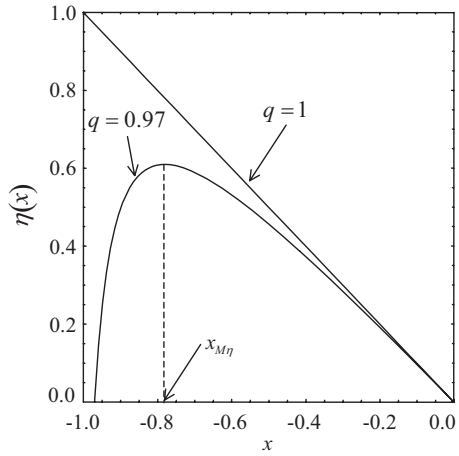

FIG. 1. Efficiency (η) vs force ratio (x) for two different fixed coupling parameters. $x_{M\eta}$ corresponds to the maximum of η for a fixed q.

tion of Eqs. (3) and (4) into Eq. (7), we obtain an expression for Φ in terms of the parameters x and q, namely

$$\Phi(x,q) = (x^2 + 2xq + 1)TL_{22}X_2^2. \tag{8}$$

This function has a minimum value at the point $x_{MDF}=-q$ for both fixed q and $TL_{22}X_2^2$ (see Fig. 2), meaning that the fraction of X_1 due to the presence of X_2 must be $X_{1MDF}=-\left(\frac{L_{12}}{L_{11}}\right)X_2$, in order to obtain a minimum dissipation steady state.

Power output. For isothermal processes of two coupled fluxes the power output is given by [13,14]

$$P(x,q) = -TJ_1X_1 = -x(x+q)TL_{22}X_2^2. \tag{9}$$

This equation corresponds to a convex curve (Fig. 2), with a maximum value at $x_{MPO}=-\frac{q}{2}$, which implies that the fraction

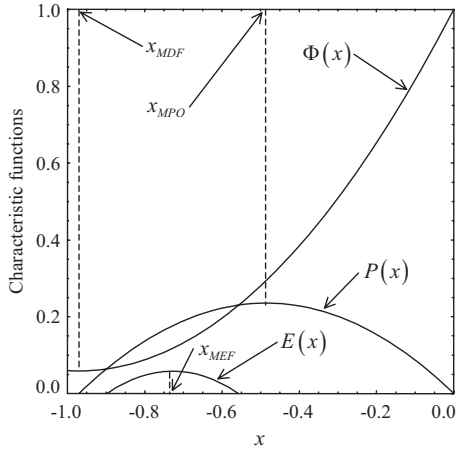

FIG. 2. Characteristic functions normalized with respect to the fixed quantity $TL_{22}X_2^2$ versus the force ratio x. Dissipation function $\Phi(x)$, power output $P(x)$, and ecological function $E(x)$, all of them for fixed $q=0.97$. $\Phi(x)$ reaches its minimum value at $x_{MDF}=-q$, $P(x)$ reaches its maximum value at $x_{MPO}=-\frac{q}{2}$, and $E(x)$ reaches its maximum value at $x_{MEF}=-\frac{3q}{4}$.

of the driven potential due to driver one in a maximum power output regime must be $X_{1MPS}=-\left(\frac{L_{12}}{2L_{11}}\right)X_2$.

The ecological function. Defining the ecological function as $E=P-\Phi$, by means of Eqs. (8) and (9), we get

$$E(x,q) = -(2x^2 + 3xq + 1)TL_{22}X_2^2. \tag{10}$$

This equation also corresponds to a convex curve with only a maximum point (Fig. 2) at $x_{MEF}=-\frac{3q}{4}$, which means that in the maximum ecological regime the relationship between the driver and driven flows must be $X_{1MEF}=-\left(\frac{3L_{12}}{4L_{11}}\right)X_2$. In this regime the conversion process undergoes a pathway accomplishing a good compromise between power output and dissipated energy, that is, for a small decrement in P we get a large decrement in $T\sigma$ [14,15].

C. Loop-shaped curves

Now, we proceed to search for LSC by using FOIT equations in an analogous way as it occurs in FTT models and actual thermal engines. The functions η [Eq. (6)], Φ [Eq. (8)], P [Eq. (9)], and E [Eq. (10)] depend on two parameters, and three of them (η, P, and E) are convex functions with respect to x. From the plots corresponding to η (Fig. 1) and P (Fig. 2), we observe that they have two zeros: for $\sqrt{L_{11}}X_1=q\sqrt{L_{22}}X_2$, corresponding to a first order steady state [17], and for $\sqrt{L_{11}}X_1 \ll q\sqrt{L_{22}}X_2$, corresponding to a totally irreversible energy transfer, and in both cases $\eta=0$. We can transform P, E, and Φ as functions of η [2,18]. From Eq. (6), we can get $x(\eta,q)$ as

$$x(\eta,q) = -\frac{q(1+\eta) \pm \sqrt{q^2(1+\eta)^2 - 4\eta}}{2}. \tag{11}$$

It is necessary to consider the two solutions of Eq. (11) because each one represents a branch of the plot x versus η for fixed q. By the substitution of Eq. (11) into Eq. (8), we get

$$\Phi(\eta,q) = \frac{(1-\eta)\{2 - q[q(1+\eta) \pm R]\}}{2}TL_{22}X_2^2, \tag{12}$$

with $R=\sqrt{q^2(1+\eta)^2-4\eta}$. On the other hand, we obtain the following expression for the power output in terms of η:

$$P(\eta,q) = \frac{\eta\{2 - q[q(1+\eta) \pm R]\}}{2}TL_{22}X_2^2. \tag{13}$$

Similarly, for the ecological function [Eq. (10)], we obtain

$$E(\eta,q) = \frac{(2\eta-1)\{2 - q[q(1+\eta) \pm R]\}}{2}TL_{22}X_2^2. \tag{14}$$

When we plot these functions versus η (Figs. 3–5 both branches) for $q \in [q_{min}, 1]$, we observe that Φ does not have a LSC behavior, while both P and E describe loop-shaped curves with some interesting points such as the maxima P and E points (η_{MPO} and η_{MEF}) and the maximum-η points ($\eta_{M\eta}$, see Figs. 4 and 5). Plots in Figs. 4 and 5 are similar to those obtained in [19] for a two-reservoir system with several irreversibilities. We will study these conspicuous points in the next section.

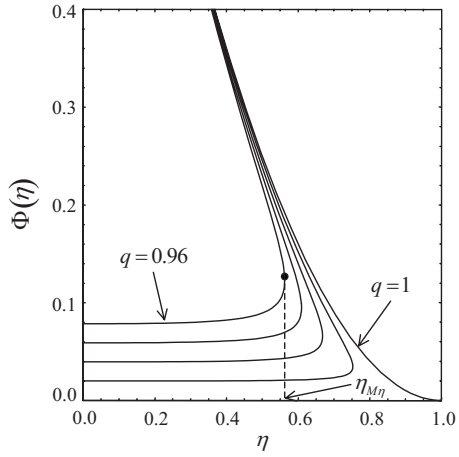

FIG. 3. Dissipation function (Φ) versus efficiency (η) for $q=1$, 0.99, 0.98, 0.97, and 0.96, respectively. $\eta_{M\eta}$ is the point which corresponds to the maximum efficiency for each case (the case $q=0.96$ is marked).

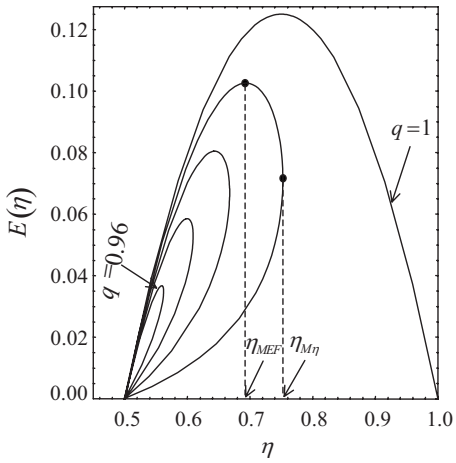

FIG. 5. Ecological function (E) versus efficiency (η) for the same q's as in Fig. 3. η_{MEF} is the point which corresponds to the maximum ecological function (the case $q=0.99$ is marked).

D. Performance modes and the coupling parameter

1. Dissipation versus efficiency

Figure 3 shows that when q decreases (i.e., the quality of the coupling diminishes), the minimum value of Φ grows and $\eta_{M\eta}$ [see Eq. (16) below] also decreases. This result may be analogous to that occurring when the heat flux through the body of a motor augments, preventing that a spontaneous flux can be used in managing a nonspontaneous one. From Fig. 3, we also see that the minimum dissipation function occurs at $\eta_{MDF}=0$, where Φ depends only on q as follows:

$$\Phi_{MDF}(\eta_{MDF}) = (1-q^2)TL_{22}X_2^2, \tag{15}$$

while the power output vanishes $P_{MDF}(\eta_{MDF})=0$ [20]. Evidently, when $q=1$, we recover the thermodynamic equilibrium state, where all of the flows vanish, that is, all interactions with the environment must be reversible processes to reach $\Phi_{MDF}(\eta_{MDF})=0$. While $\Phi_{MDF}(\eta_{MDF})\neq 0$ for any other value of q. Moreover, some authors have shown that minimum entropy production and maximum power output are inequivalent in general [21] but are equivalent under certain specific conditions [22] where internal entropy production within the working substance is not taken into account (therefore without LSC). Evidently, in the case studied here both mentioned extreme regimes are not equivalent (in Fig. 2 we see that x_{MDF} and x_{MPO} are different for any value of q).

Another interesting point is where the efficiency reaches its maximum value, which is found by means of $\partial_\Phi \eta|_{\Phi_\eta}=0$, and leads us to

$$\eta_{M\eta}(q) = \frac{q^2}{(1+\sqrt{1-q^2})^2}, \tag{16}$$

with a monotonically decreasing behavior for increasing irreversibilities ($q\to 0$) (see Fig. 6). By the substitution of Eq. (16) into Eqs. (12)–(14), we obtain functions of q only such that Φ is monotonically decreasing with q, while P and E are convex functions with only a maximum point at $q_{MPO}=\sqrt{2(\sqrt{2}-1)}\approx 0.910$ and $q_{MEF}=\sqrt{\frac{4}{3}(\sqrt{3}-1)}\approx 0.988$, respectively (see Fig. 7). The first value was found by Stucki [11] by maximizing the power output subject to the CMC derived from the assumption that the attached cellular load must be included in the entropy production [the mentioned third term, see Eqs. (34)–(36) of [11]]. Nevertheless, we show that this value ($q_{MPO}\approx 0.910$) can be obtained without considering any load, that is, by only optimizing the 2×2 *system* under maximum power output in the maximum efficiency steady state. Therefore the minimum entropy production steady state is not equivalent to a maximum efficiency steady state (see Fig. 7). The second value obtained here ($q_{MEF}\approx 0.988$) does not have equivalent in Stucki's treatment (see below and Fig. 7).

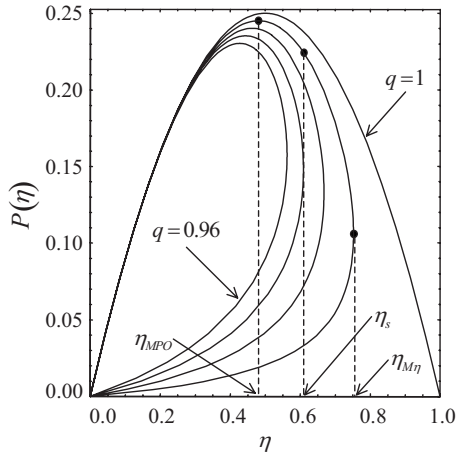

FIG. 4. Power output (P) versus efficiency (η) for the same q's as in Fig. 3. η_{MPO} and η_s are the points corresponding to the maximum power output and the semisum efficiency given by Eq. (22), respectively (the case $q=0.99$ is marked).

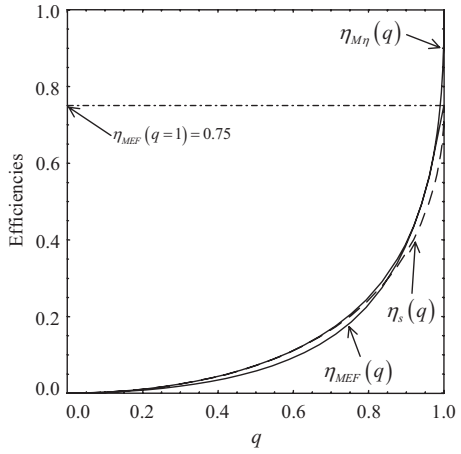

FIG. 6. Comparison between the efficiency of the $M\eta$ steady state [Eq. (16)], the efficiency of the MEF steady state [Eq. (19)], and the semisum efficiency η_s [Eq. (22), dashed curve]. $\eta_{MEF}(q=1)=0.75$ is the greatest efficiency of the MEF regime.

2. Power output versus efficiency

Figure 4 shows that for $q=1$ a parabola is obtained for $P(\eta,q)$ versus η. However, when we diminish the quality of coupling, loop-shaped curves are obtained, in which the relative position between the maxima points of power output and efficiency, respectively, depend also upon the coupling parameter q. Besides, the parabola is the boundary mark of the loop-shaped curves, that is, its maximum point gives the ideal power output when $q=1$, which is $P[\eta_{MPO}(|q|=1)]=0.25\,TL_{22}X_2^2$. This result coincides with that obtained in Ref. [18] for the muscle contraction problem.

The efficiency that maximizes the power output is obtained by means of $\partial_\eta P\eta|_{\eta_{MPO}}=0$, yielding

$$\eta_{MPO}=\frac{1}{2}\frac{q^2}{2-q^2}. \tag{17}$$

From this expression we observe that $\eta_{MPO}=\frac{1}{2}$ is reached only for $q=1$. At this point, the process variables corresponding to the MPO regime satisfy the inequality $P_{MPO}=P[\eta_{MPO}(q)]\leq\Phi_{MPO}=\Phi[\eta_{MPO}(q)]$, that is,

$$\frac{q^2}{4}TL_{22}X_2^2\leq\left(1-\frac{3}{4}q^2\right)TL_{22}X_2^2 \quad \forall\, q\in[0,1], \tag{18}$$

as it occurs in the MDF regime with the advantage that in the MPO regime the power output is not zero, which is the case for the power output in the steady state of minimum entropy production [20].

The maximum efficiency point is found by using $\partial_P\eta|_{P_\eta}=0$, which also leads to Eq. (16), and therefore the behavior of the process variables is the same as in the previous case. In Fig. 4, we see that the bigger q is the smaller $P(\eta_{M\eta})$ is, that is, when $\eta_{M\eta}$ increases, $P(\eta_{M\eta})$ decreases until the limiting case which is the parabola ($\eta_{M\eta}=1$ and $P=0$). In Fig. 4, we also see that the distance in the η axis between the maximum power and the maximum efficiency points diminishes while the quality of the coupling diminishes, reaching a null value when $q=0$. In the following paragraph, we will see how the ecological function gives a good tradeoff between maximum power and maximum efficiency.

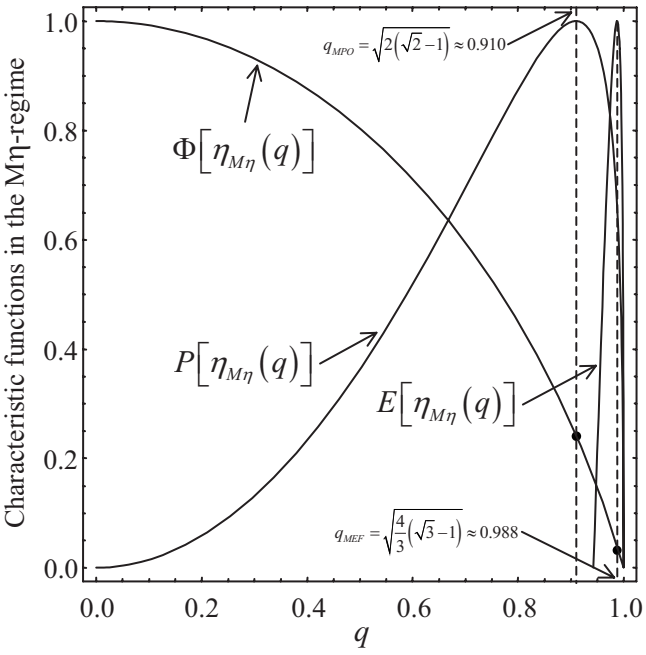

FIG. 7. Characteristic functions normalized with respect to their maximum values in terms of the coupling parameter q, at the maximum efficiency regime. For the curve $\Phi[\eta_{M\eta}(q)]$ we can observe that $q_{MPO}\approx 0.910$ (where $P[\eta_{M\eta}(q)]$ attains its maximum value) does not correspond to a minimum entropy production steady state (with $q=1$), that is, the conductance-matching condition to reach the MPO value at $\eta_{M\eta}$ regime is not necessary. Power output $P[\eta_{M\eta}(q)]$ and ecological function $E[\eta_{M\eta}(q)]$ are also depicted. $q_{MEF}\approx 0.988$ corresponds to the maximum value of $E[\eta_{M\eta}(q)]$.

3. Ecological function versus efficiency

The MPO regime provides a maximum energy output rate, but it also dissipates more energy taken from the energy input (low efficiency). Nevertheless, there exist some phenomena where this is not observed, that is, the dissipation is always smaller than the power output. In fact, many natural processes (biologic and nonbiologic) work having a good compromise between P and Φ [6,7,11,14,18,23–29]. On the other hand, as we see in Fig. 5, the ecological function [Eq. (14)] plotted versus efficiency also gives loop-shaped curves. Therefore there exists an efficiency for which one obtains the best compromise between P and Φ. This point is found by means of $\partial_\eta E|_{\eta_{MEF}}=0$, which leads to

$$\eta_{MEF}=\frac{3}{4}\frac{q^2}{4-3q^2}. \tag{19}$$

This result gives a range for q where the following inequality now is satisfied: $\Phi_{MEF}=\Phi[\eta_{MEF}(q)]\leq P_{MEF}=P[\eta_{MEF}(q)]$, that is,

$$\left(1-\frac{15}{16}q^2\right)TL_{22}X_2^2 \leq \frac{3}{16}q^2TL_{22}X_2^2; \quad \forall\, q \in \left(\frac{\sqrt{8}}{3},1\right]. \tag{20}$$

This inequality has some implications about the MEF regime. In the limit $q=1$, $\eta_{MEF}=0.75$, that is, 0.25 more than the MPO efficiency, depending on the system design. An other result is that for any value of q, $P_{MEF}=0.75\,P_{MPO}$, while the dissipation function in the case of the MEF regime suffers a drastic decrement compared to Φ_{MPO}. In fact, we have

$$\Phi_{MEF}=\frac{1}{4}\left(\frac{16-15q^2}{4-3q^2}\right)\Phi_{MPO}. \tag{21}$$

That is, within the q interval where $E>0$ $\left(q \in \left(\frac{\sqrt{8}}{3},1\right]\right)$, Φ_{MEF} goes from $0.5\,\Phi_{MPO}$ to $0.25\,\Phi_{MPO}$ [30]. To find the maximum efficiency we solve $\partial_E \eta|_{E_\eta}=0$, obtaining the same result as in the two previous regimes, that is, the maximum efficiency has the same value for all the performance regimes given by Eq. (16). Therefore we have only two q values that maximize both the power output and the ecological function in the $M\eta$ regime, that is, $q_{MPO}\approx 0.910$ and $q_{MEF}\approx 0.988$, respectively (see Fig. 7). This last value is bigger than the biggest q value (at maximum efficiency) found by Stucki corresponding to the maximization of his function $J_1X_1\eta$[11]. Let us recall that $q_{MEF}\approx 0.988$ was also found without using the CMC.

Additionally, from the loop-shaped curves of P versus η, we observe that it is possible to find an intermediate point between maximum power and maximum efficiency accomplishing a good compromise between these two ways of performance [4]. Such point is given by

$$\eta_s(q)=\frac{1}{2}[\eta_{MAX}+\eta_{MPO}]=\frac{1}{2}\left[\frac{q^2}{(1+\sqrt{1-q^2})^2}+\frac{1}{2}\frac{q^2}{2-q^2}\right]. \tag{22}$$

If we compare this expression with the MEF efficiency, η_{MEF}, we obtain the behavior shown in Fig. 6, that is, $\eta_{MEF}\approx \eta_s$. This means that the η values of the MEF regime are a good compromise between power output and maximum efficiency, which is equivalent to a low dissipation regime, with the additional fact that this occurs for a realistic $q<1$ (for example, Stucki reported a $q_{exp}\approx 0.95$ for liver mitochondria from male rats [11]). However, some authors have considered the ideal case $q=1$ to study some ATP problems [26].

III. ON ATP PRODUCTION: A LINEAR APPROACH

The purpose of this section is to apply methodology presented in Sec. II. One of the most important examples of the energy conversion in biology is the aerobic ATP synthesis (see Refs. [23,25–29]). The global chemical reaction of ATP synthesis is given by [23]

$$\{C_6H_{12}O_6+6O_2+6H_2O\}+[36ADP+36P^+] \rightleftharpoons \{6CO_2+12H_2O\}+[36ATP], \tag{23}$$

where driver and driven reactions have been indicated with curly and square brackets, respectively. For the spontaneous reaction we take $J_2X_2>0$ and for the nonspontaneous one, $J_1X_1<0$. Some experiments suggest that this process occurs out but near an equilibrium state [6,11,23]. Thus we can use the formalism of Sec. II. Stucki considered as a reasonable idea that *in vivo* oxidative phosphorylation operates simultaneously at both maximum efficiency and minimum entropy production. This situation in Stucki's words is reached in a steady state named conductance matching between extreme states of zero and infinite conductances, respectively [11]. However, as it can be observed in Fig. 4 [which stems from the parametric combination of Eqs. (6) and (9) for realistic values of $|q|<1$], there exists a unique point with simultaneous zero values for η and P (which corresponds to the minimum entropy production steady state, see Fig. 3). Thus a conductance-matching condition in Stucki's sense is not necessary for $q<1$. Among the four objective functions proposed in [11], the one given by $F_S=J_1X_1\eta$ at maximum efficiency, is in Stucki's words, the most suitable for the oxidative phosphorylation case. The optimal efficiency obtained with this function is $\eta_F=0.618$ derived with a coupling parameter of $q_p^{ec}\approx 0.972$ [Eq. (58) in Ref. [11]]. This η_F value is lower than those reported efficiencies calculated from actual free energy changes, which are larger than their corresponding standard free energy changes for biochemical reactions like Eq. (23). In fact, for ATP synthesis under *in vivo* conditions the efficiency can be around 0.736 [31,32]. Remarkably, these values $\eta_F=0.618$ and $q_p^{ec}\approx 0.972$ can be also obtained with the 2×2 energy conversion formalism without using the CMC in the following way: by the substitution of $\eta_{M\eta}$ given by Eq. (16) into the power output [Eq. (13)] and multiplying again by $\eta_{M\eta}$ we get $F_S(\eta_{M\eta})$ (the so-called "efficient power" [33] in the maximum efficiency steady state), which corresponds to a convex curve with a maximum at $q\approx 0.972$ (i.e., q_p^{ec}). By substituting this q value into Eq. (16) we obtain the same $\eta_F=0.618$ (without CMC). Thus we obtained these results for $\eta_{M\eta}$ and q_p^{ec}, and that of Sec. II D 1 for $q_p\approx 0.910$ by using only a 2×2 formalism. In fact, all of the Stucki results of his Table I [11] for four economic degrees of coupling can be obtained by the same procedure without recurring to the CMC.

If we take the efficiency value, provided by the FOIT formalism, as a good criterion to choose the objective function at which oxidative phosphorylation thermodynamically performs, then we can propose as the objective function the ecological one due to its previously discussed properties. The "efficient power" ($F_S=J_1X_1\eta$) used by Stucki [11] leads to $\eta_F=0.618$. However, Nelson and Cox (see Box 13.1 of [31], p. 498) reported that oxidative phosporylation under *in vivo* conditions can reach efficiencies as high as 0.736 since actual free energy changes are larger than their corresponding standard free energy changes. From Fig. 4, it can be seen that along the LSC between the maximum power output point and the maximum efficiency point, there is an infinite number of points corresponding each one of them to a particular mode of operation. Among these points one could choose some of them in terms of their energetic properties, such as a good compromise between high power output and low

dissipation [4,34]. One mode of performance that accomplishes this goal is the so-called ecological function (see Sec. II D 3). If we use the ecological function at maximum efficiency, which is analogous to the "economic" functions of Stucki, we find for the MEF regime, $q_{MEF}\approx 0.988$ (see Secs. II D 1 and II D 3). If we substitute this value into the expression for the maximum efficiency, Eq. (16), we get $\eta_{MEF}=0.732$, which is close to the estimated actual efficiency values [31,32]. We use a compromise function $C(q)$ of the type defined in [34] to compare the thermodynamic performance of the ecological function ($q_{MEF}\approx 0.988$) with the efficient power ($q_p^{ec}\approx 0.972$). This function in terms of normalized quantities with respect to the MPO regime at optimum efficiency is given by

$$C(q)=\frac{P[\eta_{M\eta}(q)]}{P[\eta_{M\eta}(q_{MPO})]}-\frac{\Phi[\eta_{M\eta}(q)]}{\Phi[\eta_{M\eta}(q_{MPO})]}. \tag{24}$$

The function $C(q)$ has a maximum at $q_C\approx 0.982$, and it represents the best compromise between high power output and low dissipation. If this function is evaluated in q_p^{ec}, one obtains $C(q_p^{ec})=0.479$. On the other hand, for q_{MEF}, one obtains $C(q_{MEF})=0.489$, that is, a slightly larger value than $C(q_p^{ec})$. However, in percentage terms q_{MEF} is twice closer to $q_C\approx 0.982$ than q_p^{ec}. Thus the ecological optimization provides a reasonable criterion for the thermodynamical performance of oxidative phosphorylation (without CMC), with the advantage of giving a higher efficiency value within the range of actual values.

IV. CONCLUDING REMARKS

In the present paper, we have developed a procedure to study an irreversible linear energy converter that works under several steady-state conditions, by using optimization criteria stemming from nonequilibrium approaches [35]. Such criteria enhance the information given by the FOIT formalism. In this way, it is possible to describe the mutual influence between the operating mode of the energy converter (generalized forces and fluxes) and its design (phenomenological Onsager coefficients). Thus we get some insights about the quantitative description of the energetics of a 2×2 *system*.

Our results allow one to see that the FOIT formalism along with FTT procedures lead to loop-shaped curves such as it is observed in actual dissipative thermal engines [2,3] and some biological systems (for instance, in the case of experimental data of efficiency versus power output reported by Smith *et al.* [25] for the soleous muscle of mouse). Our thermodynamic approach connects FOIT and some concepts arising from finite-time thermodynamics [35]. However, our approach is somewhat different to that suggested by Verhas and de Vos [36].

Finally, in this work we have obtained all of Stucki's results [11] for the optimal efficiency and the economic degrees of coupling of oxidative phosphorylation by using only a 2×2 coupled system of fluxes without assuming the so-called conductance matching condition. Therefore our approach suggests that the minimum entropy production regime is not compatible with the optimal efficiency steady state. In fact the MEP regime leads to both zero efficiency and zero power output. On the other hand, we found that the so-called maximum ecological regime is suitable for the energetic description of oxidative phosphorylation, since this criterion gives a high efficiency value within the range of actual efficiencies. In addition, this regime represents a good compromise between high power output and low dissipation. In summary, our results indicate that the role played by the attached cellular load is not necessary for the energetic description of the two coupled fluxes involved in the biochemical reaction of ATP synthesis, in the same way that no particular load is necessary to describe the internal energetics properties of a typical power plant. If one wishes to take into account the external load, a 3×3 formalism is necessary for the overall thermodynamic description of the complete system, leading to a new set of energetic equations different from Eqs. (5) and (9).

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