A first–order irreversible thermodynamic approach to a simple
energy converter

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Abstract

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 against 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 ATP–synthesis within mitochondrias. In that work the author did not use the mentioned loop–shaped curves and he proposed that oxidative phosphorylation operates in a steady state simultaneously at minimum entropy production and maximum efficiency, 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 in the simultaneous maximization of 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 is common to find irreversibilities (losses) due to friction and irreversible heat fluxes. These losses must be taken into account in the models elaborated to describe their general performance. In the thermal engine modeling this kind 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 (Section II), we show that in the case of a linear energy converter consisting of two coupled fluxes described by FOIT, in which one spontaneous flow manages a nonspontaneous one, loop–shaped curves (LSC) similar to those appearing in irreversible thermal engine models can be also obtained. These LSC for our FOIT–model are obtained for both power output \((P)\) versus efficiency \((\eta)\) and for ecological function \((E)\) versus \(\eta\), with ecological function defined as the power output minus the dissipation function \((T\sigma, \text{see subsection II B})\) \[4\]. In both loop–shaped curves it appears a force ratio given by \[5\],

\[
x = \sqrt{\frac{L_{11}}{L_{22}}} X_1 X_2,
\]

(1)

(with \(L_{ij}\) being 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,

\[
q = \frac{L_{12}}{\sqrt{L_{11}L_{22}}}.
\]

(2)

This parameter gives us a measure of the coupling of spontaneous and nonspontaneous fluxes \[6\]. In section II we also show that by means of the LSC properties we can study...
several performance modes of the energy converter similar to those used in Finite Time Thermodynamics (FTT)\cite{7,8,9,10}, but with further results which consist in a set of functions describing how the maxima points can move one respect to the other. As an example of our previous results, we study the ATP production occurring within mitochondria by means of respiration. A FOIT–approach to this problem was previously published by Stucki\cite{11}. The Stucki’s approach was mainly based on using two fluxes and two forces subject to several optimization criteria proposed by this author. The 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 which simultaneously corresponds to a maximum efficiency state. This last situation stems from the so–called conductance–matching condition (CMC), which is obtained by means of the inclusion of a third term in the expression for the entropy production, which corresponds to an attached cellular load under steady state conditions. The phenomenological coefficient of the third term mentioned can be fitted to obtain that the minima values of entropy production coincide with the optimum values of efficiency. Stucki uses several objective functions to model different mitochondria modes of operation but only by using the former two forces and two fluxes system and by 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 means that the attached load is not necessary to describe the energetics of a linear energy converter consisting in a pair of coupled processes where one drives the other. In summary, in this article 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 here obtained without the usage of the attached cellular load. If the Stucki’s third term in the entropy production is considered, then the energetics formalism should be rewritten in terms of a 3 x 3 matrix of phenomenological coefficients, with its consequent changes in quantities such as the efficiency and the power output. This paper is organized as follows: In section II we discussed on the energetics of a 2 x 2 system; In section III we applied some of the results of the previous section on the ATP–production under a linear approach. Finally in section IV we present some concluding remarks.
II. ON THE 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 show some new ones. In particular, we will show that a linear isothermal–isobaric engine working in the MEF–regime can reach an efficiency until $\eta_{MEF} = 0.75$.

A. Constitutive equations

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

\begin{align}
J_1 &= \sqrt{L_{11}} \left( \sqrt{L_{11}} X_1 + q \sqrt{L_{22}} X_2 \right) \\
J_2 &= \sqrt{L_{22}} \left( q \sqrt{L_{11}} X_1 + \sqrt{L_{22}} X_2 \right),
\end{align}

FIG. 1: Efficiency ($\eta$) vs. force ratio ($x$) for two different fixed coupling parameters. $x_{MQ}$ corresponds to the maximum of $\eta$ for a fixed $q$. 
with $L_{12} = L_{21}$, the symmetry Onsager relation between crossed coefficients. In these equations we use the coupling coefficient defined by Eq. (2) [6]. Thus, in the limit case $q \to 0$, 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 $q \to 1$, 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 both 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,

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

From Eq. (1), we get an expression for $\eta$ in terms of $x$ and $q$ as follows,

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

A plot of $\eta$ versus $x$ for a fixed $q$ is depicted in Figure 1. This graph is a convex curve with only a maximum point. That is, there exists a relation 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 according to a certain objective function maximization. First, we calculate the following characteristic functions: the dissipation function, the power output and the ecological function.

### B. Characteristic functions

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

$$
\sigma = J_1 X_1 + J_2 X_2,
$$

(7)
FIG. 2: Characteristic functions normalized 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 $x_{MEF} = -\frac{3q}{4}$.

and following Tribus [5], the dissipation function for an isothermal system can be expressed as $\Phi = T\sigma$. By the substitution of Eqs. (3) and (4) into Eq. (7), in terms of the parameters $x$ and $q$, $\Phi$ becomes,

$$\Phi(x, q) = \left(x^2 + 2qx + 1\right) TL_{22}X_2^2.$$  

(8)

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

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

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

(9)

This equation corresponds to a convex curve (Figure 2), with a maximum value at $x_{MPO} = -\frac{q}{2}$, this condition implies that the fraction of the driven potential due to driver one in a maximum power output regime must be $X_{1MPS} = -\left(\frac{L_{12}}{2L_{11}}\right) X_2$. 

7
**The Ecological function.**- Defining the ecological function as $E = P - \Phi$, by means of Eqs. (9) and (8), we get

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

This equation also corresponds to a convex curve with only a maximum point (Figure 2) at $x_{MEF} = -\frac{3q}{4}$, this means that in the maximum ecological regime the relation between the driver and driven flows must be $X_{1,MEF} = -\left(\frac{3L_{22}}{L_{11}}\right)X_2$. In this regime the conversion process undergoes a pathway accomplishing a good compromise between power output and dissipated energy, that is, with a small decrement in $P$ we get a great decrement in $T\sigma$. [14, 15].

C. **Loop–shaped plots**

Here, we find LSC by using FOIT-equations in an analogous way as it occurs in FTT–models and actual thermal engines. The functions $\eta$ (Eq. 6), $\Phi$ (Eq. 8), $P$ (Eq. 9) and $E$ (Eq. 10) depend on two parameters, and three of them ($\eta$, $P$ and $E$) are convex functions with respect to $x$. From the plots corresponding to $\eta$ (Figure 1) and $P$ (Figure 2), we observe they have two zeros: when $\sqrt{L_{11}X_1} = q\sqrt{L_{22}X_2}$, corresponding to a first order steady state [18], and when $\sqrt{L_{11}X_1} << q\sqrt{L_{22}X_2}$ corresponding to a totally irreversible energy transfer, in both cases $\eta = 0$. We can transform $P$, $E$ and $\Phi$ as functions of $\eta$ [2, 19]. By means of Eq. (6), we first get $x(\eta, q)$ as

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

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

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

with $R = \sqrt{q^2(1 + \eta)^2 - 4\eta}$. For the power output (Eq. 9) we obtain

$$P(\eta, q) = \eta\left(2 - q\left[q(1 + \eta) \pm R\right]\right)TL_{22}X_2^2,$$ \hspace{1cm} (13)

and in the same way, for the ecological function (Eq. 10), we have

$$E(\eta, q) = \left(2\eta - 1\right)\left(2 - q\left[q(1 + \eta) \pm R\right]\right)TL_{22}X_2^2.$$ \hspace{1cm} (14)
FIG. 3: Dissipation function ($\Phi$) versus efficiency ($\eta$) for $q = 1, 0.99, 0.98, 0.97, 0.96$ respectively. $\eta_{Mq}$ is the point which corresponds to the maximum efficiency for each case (here the case $q = 0.96$ is marked).

When we plot these functions against $\eta$ (Figures 3, 4 and 5, both branches) for $q \in [q_{\min}, 1]$, we observe that $\Phi$ has a monotonically decreasing behavior, but $P$ and $E$ describe loop–shaped curves with some interesting points: the maxima $P$ and $E$ points ($\eta_{MPO}$ and $\eta_{MEF}$) and the maximum–$\eta$ points ($\eta_{M\eta}$, see Figures 4 and 5). Plots in Figures 4 and 5 are similar to those obtained in [20] for a two–reservoir system with several irreversibilities. We will study these conspicuous points in next subsection.

D. Performance modes and the coupling parameter

1. Dissipation versus efficiency

In Figure 3 we observe that while $q$ decreases (i.e. the quality of the coupling diminishes), the minimum value of $\Phi$ augments and $\eta_{M\eta}$ (see Eq. (16) below) also decreases. This result may be the analogous of 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. In Figure 3 we see that the minimum dissipation function occurs at $\eta_{MDF} = 0$, where
FIG. 4: Power output ($P$) versus efficiency ($\eta$) for the same $q'$s as in Figure 3. $\eta_{Mpo}$ and $\eta_s$ are the points corresponding to the maximum power output and the semisum efficiency given by Eq. (22), respectively (here the case $q = 0.99$ is marked).

$\Phi$ only depends on $q$ as

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

while the power output vanishes $P_{MDF}(\eta_{MDF}) = 0$ \[21\]. Evidently, when $q = 1$, we recover the thermodynamic equilibrium state, where all of the flows vanish, that is, to reach $\Phi_{MDF}(\eta_{MDF}) = 0$ all interactions with the environment must be reversible processes. For any other value of $q$, $\Phi_{MDF}(\eta_{MDF}) \neq 0$.

Another point of interest is that where the efficiency reaches its maximum value, which is found by means of $\partial\Phi\eta\mid_{\Phi_{\eta}} = 0$, and lead us to

$$\eta_{Mq}(q) = \frac{q^2}{(1 + \sqrt{1 - q^2})^2},$$

with a monotonically decreasing behavior while the irreversibilities increase ($q \to 0$, see Figure 6). By the substitution of Eq. (16) into Eqs. (12), (13) and (14), we obtain only functions of $q$ such that $\Phi$ 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 $q_{MEF} = \ldots$
FIG. 5: Ecological function \( (E) \) versus efficiency \( (\eta) \) for the same \( q' \)'s as in Figure 3. \( \eta_{MEF} \) is the point which corresponds to the maximum ecological function (here the case \( q = 0.99 \) is marked).

\[
\sqrt{\frac{1}{3} (\sqrt{3} - 1)} \approx 0.988, \text{ respectively (see Figure[7]). The first value was found by Stucki (see eq. 52 of [11]) by maximizing the objective function given by its equation 48 [11] (that is, the power output) subject to the CMC obtained from his assumption that the attached cellular load must be included in the entropy production (the mentioned third term, see eqs. 34, 35 and 36 of [11]). Nevertheless, here we show that this value \( (q_{MPO} \approx 0.910) \) can be obtained without considering any load, that is, by only optimizing the 2 x 2 system under maximum power output in the maximum efficiency–steady state. Then the minimum entropy production steady state is not equivalent to a maximum efficiency steady state (see Figure[7]). The second value \( (q_{MEF} \approx 0.988) \) has not an equivalent in the Stucki’s treatment (see below and Figure[7]).

2. Power output versus efficiency

The graph of \( P(\eta, q) \) versus \( \eta \) (see Figure[4]) shows that for \( q = 1 \) a parabola is obtained. 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 re-
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 $\eta_s$ (Eq. (22), dashed curve). $\eta_{MEF} (q = 1) = 0.75$ is the greatest efficiency of the MEF–regime.

spectively also depend on 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 $P [\eta_{MPO} (|q| = 1)] = 0.25 \times TL_{22}X_2^2$. This result coincides with that of ref. [19] for the muscle contraction problem.

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

$$\eta_{MPO} = \frac{1}{2} \frac{q^2}{2 - q^2}. \quad (17)$$

Here, we observe that only for $q = 1$, $\eta_{MPO} = \frac{1}{2}$. 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,

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

as it occurs in the MDF–regime with the advantage that in this MPO–regime the power output is not zero, as it is the case for the power output in the minimum entropy production steady state [21].
FIG. 7: Characteristic functions normalized respect to their maximum values in terms of the coupling parameter $q$, at the maximum efficiency regime. For the curve $\Phi[\eta_M(q)]$ we can observe that $q_{MPO} \approx 0.910$ (where $P[\eta_M(q)]$ 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 $\eta_M$–regime is not necessary. Power output $P[\eta_M(q)]$ and Ecological function $E[\eta_M(q)]$ are also depicted. $q_{MEF} \approx 0.988$ corresponds to the maximum value of $E[\eta_M(q)]$.

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 Figure 4 we see that the bigger $q$ the smaller $P(\eta_M)$, that is, when $\eta_M$ increases $P(\eta_M)$ decreases until the limit case of the parabola ($\eta_M = 1$ and $P = 0$). In Figure 4 we also see that the distance in the $\eta$–axis between the maximum power and the maximum efficiency points diminishes while the quality of the coupling diminishes and reaches 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.
3. Ecological function versus efficiency

The MPO–regime provides a maximum energy output rate, but also produces a great energy dissipation 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 following a good compromise between $P$ and $\Phi$ \[6, 7, 11, 14, 19, 22, 23, 24, 25, 26, 27, 28\]. On the other hand, as we see in Figure 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 $\Phi$. This point is found by means of $\partial q E|_{\eta_{MEF}} = 0$, which leads to

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

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

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

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’s design. Other result is that for any value of $q$, $P_{MEF} = 0.75 \times P_{MPO}$, while the dissipation function in the case of MEF–regime suffers a drastic decreasing compared with $\Phi_{MPO}$. In fact we have

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

That is, within the $q$–interval where $E > 0$ ($q \in \left(\frac{\sqrt{8}}{3}, 1\right)$), $\Phi_{MEF}$ goes from $0.5 \times \Phi_{MPO}$ to $0.25 \times \Phi_{MPO}$. To find the maximum efficiency we solve $\partial E|_{E_n} = 0$, obtaining the same result that in the two previous regimes, that is, the maximum efficiency has the same value for all of 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 Figure 7). This last value is bigger than the biggest $q$–value (at maximum efficiency) found by Stucki corresponding to the maximization of his function $J_1 X_1 \eta$ \[11\]. $q_{MEF} \approx 0.988$ was also found without using the CMC.
Additionally, in the loop–shaped curves of $P$ versus $\eta$, 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 \[4\]. This point is

$$
\eta_s (q) = \frac{1}{2} [\eta_{MAX} + \eta_{MPO}]
$$

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

If we compare this expression with the MEF–efficiency, $\eta_{MEF}$, we obtain the behavior shown in Figure 6, that is, $\eta_{MEF} \approx \eta_s$. This means that the $\eta$ 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 \[25\] have considered the ideal case $q = 1$ to study some ATP problems.

III. ON ATP PRODUCTION: A LINEAR APPROACH

The purpose of this section is an application of the methodology presented in Section \[II\]. One of the most important examples of the energy conversion in biology is the aerobic ATP–synthesis (see references \[22, 24, 25, 26, 27, 28\]). The global chemical reaction of ATP synthesis is given by \[22\],

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

where driver and driven reactions have been indicated with curly and square brackets, respectively. For the spontaneous reaction we take $J_2 X_2 > 0$ and for the nonspontaneous one, $J_1 X_1 < 0$. Some experiments suggest this process occurs out but near an equilibrium state \[6, 11, 22\], thus, we can use the formalism of Section \[II\]. Stucki considered as a reasonable idea that in vivo oxidative phosphorylation simultaneously operates 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 Figure 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 $\eta$ and $P$ (which corresponds to the minimum entropy production steady state, see Figure 3). Thus, for $q < 1$ a conductance–matching condition in the Stucki’s sense is not necessary. Among the four objective functions proposed in [11], that given by $F_S = J_1 X_1 \eta$ at maximum efficiency, is in Stucki’s words the most suitable for the oxidative phosphorylation case. The optimal efficiency obtained with this function is $\eta_F = 0.618$ arising from a coupling parameter of $q_p^{ec} \approx 0.972$ (his Eq. (58)).

This $\eta_F$ value is lower than reported efficiencies calculated from actual free energy changes, which are larger than their corresponding standard free energy changes for biochemical reactions as 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 x 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 subsubsection II D 1 for $q_p \approx 0.910$ by using only a 2 x 2 formalism. In fact, all of the Stucki results of his Table I [11] for his 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 choice the objective function at which oxidative phosphorylation thermodynamically performs, then we can propose as objective function the ecological one due to its properties previously discussed. The efficient power ($F_S = J_1 X_1 \eta$) used by Stucki [11] leads to $\eta_F = 0.618$. However, Nelson and Cox (see Box 13.1 of [31], pag. 498) reported that oxidative phosphorylation under in vivo conditions can reach efficiencies as high as 0.736 due to actual free energy changes are larger than their corresponding standard free energy changes. If one observes Figure 4 along the LSC between the maximum power output point and the maximum efficiency point, one has an infinite number of points corresponding each one of them to a particular mode of performance. Among these points one can choice some of them in terms of their energetic properties, such as a good compromise between high power output and low dissipation [4, 17]. One mode of performance that accomplishes this goal is the so–called ecological function (see subsubsection 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, \( q_{\text{MEF}} \approx 0.988 \) (see subsubsections II D 1 and II D 3). If we substitute this value into Eq. (16) (the expression for the maximum efficiency) we get \( \eta_{\text{MEF}} = 0.732 \), which is near estimated actual efficiency values \([31, 32]\). To compare the thermodynamic performance of the ecological function \( q_{\text{MEF}} \approx 0.988 \) with the efficient power \( q_{\text{ec}} \approx 0.972 \) we use a compromise function \( C(q) \) of the type defined in \([17]\). This function in terms of normalized quantities respect to the MPO–regime at optimum efficiency is given by

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

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 \( q_{\text{ec}} \), then \( C(q_{\text{ec}}) = 0.479 \). On the other hand, for \( q_{\text{MEF}} \), \( C(q_{\text{MEF}}) = 0.489 \), that is, a slightly larger value than \( C(q_{\text{ec}}) \). However, in percentage terms \( q_{\text{MEF}} \) is twice closer to \( q_C \approx 0.982 \) than \( q_{\text{ec}} \). Thus, the ecological optimization provides a reasonable criterion for the thermodynamical performance of oxidative phosphorylation (without CMC), with the advantage of giving a high 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 working under several steady–state conditions, by using optimization criteria stemming from some non–equilibrium approaches \([29]\). Such criteria enhance the information given by the FOIT–formalism. In this way, one can 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 \( \times \) 2 system.

Our results permit 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 as it is the case of experimental data of efficiency versus power output reported by Smith et al \([24]\) for the soleous muscle of mouse. Our thermodynamic approach to the bridge between FOIT and some concepts arising from finite–time thermodynamics \([29]\) are somewhat different to that suggested by Verhas and de Vos \([30]\).
Finally, in this work we have obtained all of the Stucki's results [11] for the optimal efficiency and the economic degrees of coupling of oxidative phosphorylation by using only a $2 \times 2$ coupled system of fluxes without resorting 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 $3 \times 3$ formalism is necessary for the overall thermodynamic description of the complete system, leading to a new set of energetic equations different to those as eqs. (5) and (9).

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