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A variational approach to the control of electrochemical hydrogen reactions

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Abstract

Optimal control problems for the hydrogen evolution reaction (HER) system are solved for different cost objectives and admissible control strategies. The solution for the set-point-change process is given in analytical terms when the admissible controls are continuous functions of time. For piecewise-continuous controls the problem admits a solution as a feedback law. In both cases the cost functional penalizes the electrochemical power spent in the process, which translates into a Lagrangian more involved than classical quadratic. The theoretical framework remains into the Calculus of Variations for infinite-horizon problems. The Hamiltonian control formalism is adapted to treat the problem when the final time is bounded.

Keywords: Process control; Optimization; Nonlinear dynamics; Electrochemistry; Hydrogen evolution reaction; Hydrogen technology

1. Introduction

Hydrogen evolution reactions (HER) are commonly referred to when electrochemical processes with hydrogen production or consumption are occurring. Typical HER processes are electrolysis, where electrical energy is supplied in order to decompose the water molecule into gaseous H_2 and O_2; and fuel cells operation, where the reverse combination is conducted in a controlled setup to produce electricity. These processes are receiving increasing attention given the recurrent crisis in oil prices, the search for clean energy sources to mitigate global warming, and the current rate of depletion of natural fuels. But there exists an extensive bibliography on other fields of research applying HER equations, for instance in cold nuclear fusion (Green and Britz, 1996; Yang and Pyun, 1996), or in the H_2-decontamination and corrosion of heavy metals (see Al-Faqeer and Pickering (2001), and a review paper in preparation). Therefore, a continuous theoretical activity on the modeling and simulation of HER kinetics is acknowledged. Since these reactions usually evolve on the surface of metallic electrodes, experimental work is also being developed to determine kinetic parameters for different cathodes (Ni, Pt, Pd, Co_3O_4) and environments (acidic or alkaline solutions). But also, as new applications of hydrogen technology are announced, interest is growing in the design, operation, and optimization of industrial devices based on HER systems. In this paper, the control of HER equations with fixed parameter values is attacked. A deterministic process control point of view is adopted, and some problems are posed and discussed in the realms of Calculus of Variations (Gelfand and Fomin, 1963) and Optimal Control (Kalman et al., 1969; Sontag, 1998).

The dynamics of HER are irreducibly nonlinear. This is confirmed by the detection of solution trajectories whose qualitative characteristics are only possible for nonlinear systems (see the extensive review by Hudson and Tsotsis, 1994). Simulations and experiments have shown hysteresis-like cyclic behaviors (Costanza et al., 2003), bistability (see Section 6), strange attractors and chaos (Green et al., 2000). These somehow unexpected experimental results shed insight over the theory of adsorption mechanisms,

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spatiotemporal patterns of catalytic electrodes, and related physical problems.

Parameter variation strategies are being developed by other researchers to avoid or to cope with these complexities in electrochemical systems (see for instance Kiss et al., 1997; Parmananda et al., 1999), and ultimately to make safe the operation of emerging industrial applications. Here the overpotential will play the role of a manipulated or control variable, but the parameters will remain constant. Basically, two different sets of admissible controls will be considered: (i) strictly continuous, piecewise-differentiable time-functions (related to the *RC*-approximation discussed in Section 4), and (ii) just piecewise-differentiable, eventually discontinuous trajectories (Section 5 and further).

Emphasis will be put on the optimal control of the transient process occurring during set-point changes. Regulation problems, more related to stability analysis, have an intrinsic local character which allows the dynamics to be approximated by linear or “quasi-linear” control models. But set-point changes involve large departures of the state variables from one equilibrium (the original steady-state), until reaching another equilibrium (the target), so the nonlinearity of the dynamics should be wholly considered.

In the next section, the physical context of the dynamical system underlying the problem is succinctly presented through balance equations. In Section 3 the tracking formalism describing the control of set-point changes in continuous processes (Costanza, 1997; Costanza and Neuman, 2000) is rephrased for this case, and different optimization criteria for evaluating the VHT electrochemical performance are discussed. In Section 4 the variational approach (the use of Calculus of Variations’ basic results) appears as the appropriate mathematical tool to solve an optimization problem posed on some approximate dynamics, namely the *RC*-circuit reduced analogue of the original VHT-system. The solution is sought amongst a subset of the time schedules commonly accepted for control variables in engineering processes. The reason for restricting the admissible control strategies to the piecewise-differentiable but strictly continuous functions of time comes from the eventual applicability of this approximation to batteries’ dynamics, where the electrical overpotential variation may be interlocked with mass transport phenomena (Vincent and Scrosati, 1997).

The variational approach turns however to be useful also in dealing with the VHT-equations under discontinuous controls. After a suitable change of variables, which is discussed in Section 5, the main result of the paper, consisting of a feedback-law-based control algorithm for set-point change evolutions of the original system under general admissible manipulations, is devised and illustrated. This algorithm is optimal in infinite-horizon situations, and suboptimal in general.

Stochastic aspects of the optimal control problem have not been discussed in this paper. However, given their importance in real-life situations, the problem will be treated in forthcoming articles. A first step towards control robustness will appear in Costanza (2005). The model can be updated through recursive procedures involving approximate realizations of increasing dimension, similar to Isidori’s approach to feedback design for global robust stability (see Isidori, 1999). Noise in signals can then be treated by using previous results on extensions of Kalman filters to bilinear systems (advanced in Costanza and Neuman, 1995).

In Section 6 the phase-space flow of the pair (state, input) variables under different time-horizon constrains is numerically approximated, and the main qualitative results are discussed, in view to the design of more accurate strategies for finite horizon problems. The basis for an alternative method to treat these problems through the Hamiltonian formalism, introducing a new (costate) variable that satisfies an (adjoint) ODE coupled to the original dynamics, and a final boundary condition, is presented in Section 7. The last section is devoted to summarize the conclusions.

2. Description of the system. The Volmer–Heyrovsky–Tafel steps. Dynamic simulations

The dynamics of hydrogen adsorption, desorption, and chemical reactions over the surface of an electrode is usually modelled through a combination of three elementary “steps” (Gennero de Chialvo and Chialvo, 1996, 1998), with corresponding velocities:

Volmer: $$H_2O + e^- \rightleftharpoons H_{(ads)} + OH^-, \tag{1a}$$

$$v_V = v_V^e \left\{ \frac{1-\theta}{1-\theta_e} e^{-(1-\alpha) f \eta} - \frac{\theta}{\theta_e} e^{\alpha f \eta} \right\}, \tag{1b}$$

Heyrovsky: $$H_2O + H_{(ads)} + e^- \rightleftharpoons H_{2(g)} + OH^-, \tag{2a}$$

$$v_H = v_H^e \left\{ \frac{\theta}{\theta_e} e^{-(1-\alpha) f \eta} - \frac{1-\theta}{1-\theta_e} e^{\alpha f \eta} \right\}, \tag{2b}$$

Tafel: $$H_{(ads)} + H_{(ads)} \rightleftharpoons H_{2(g)}, \tag{3a}$$

$$v_T = v_T^e \left\{ \left(\frac{\theta}{\theta_e} \right)^2 - \left(\frac{1-\theta}{1-\theta_e} \right)^2 \right\}, \tag{3b}$$

where the main variables involved are: θ is the surface coverage (the fraction of the electrode surface covered by adsorbed atomic hydrogen $H_{(ads)}$), and η the overpotential imposed on the system to run the reaction. Other symbols and parameters used mean: $H_{2(g)}$ is gaseous (desorbed) molecular hydrogen, v_V^e, v_H^e, v_T^e are equilibrium reaction rates of each step, θ_e is the specific equilibrium surface coverage ($\theta_e = 0.1$ in numerical calculations and graphics of this paper), α is adsorption symmetric factor (=0.5 in calculations), R is gas constant = 8.3145 J mol^{-1} K^{-1}, F is Faraday constant = 96484.6 C mol^{-1}, T is absolute temperature, here taken equal to 303.15 K and $f = F/RT = 38.2795$ C J^{-1}.

By taking all three routes into account, and assuming that the electrode’s surface coverage is proportional to the

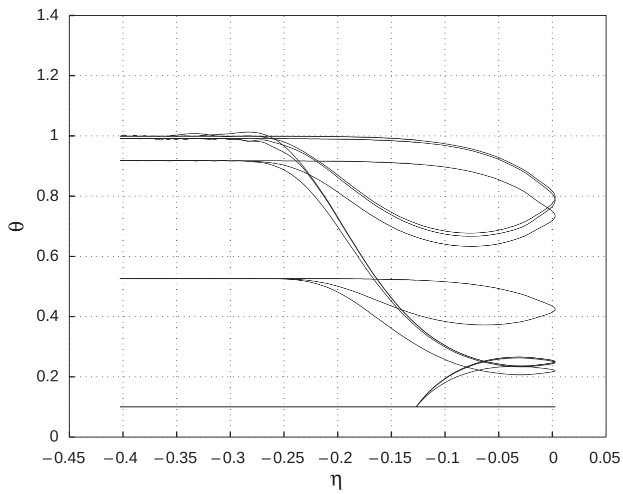

Fig. 1. Hysteresis in phase-space. Parameter values: $v_V^e = 10^{-10}$, $v_T^e = 0$, $v_H^e = 10^{-10}, 10^{-11}, 10^{-12}, 10^{-13}, 10^{-14}$ (from top to bottom).

number of atoms of $H_{(ads)}$, then the HER stoichiometric balance translates into a θ accumulation rate equation:

$$\dot{\theta} = \frac{F}{\sigma}(v_V - v_H - 2v_T), \quad \left(\triangleq g(\theta, \eta)\right), \tag{4}$$

where σ is the experimentally measured surface density of electric charge to complete a monolayer coverage of $H_{(ads)}$. In the numerical results of this paper a value of $\sigma = 2.21 \times 10^{-4}\,\mathrm{C\,cm^{-2}}$ will be adopted, corresponding to a standard Pt electrode (similar to Harrington and Conway, 1987).

Typical solutions for a toothed periodic path given to the forcing voltage η are illustrated in Figs. 1 and 4. Hysteresis loops can be observed in Fig. 1 for most of the reference velocities used in these calculations, but such qualitative behavior is not present in other regions belonging to the range of admissible values for v_V^e, v_H^e, v_T^e. One of the reasons for making set-point changes desirable might be just to avoid regions where hysteresis can appear.

Sometimes a "double layer" capacitance is proposed to explain the overpotential decay when the circuit is opened (see Harrington and Conway, 1987). In this paper only close-circuit situations will be considered, so at each time t the overpotential will be allowed to assume any admissible value $\eta(t)$, independently of the value of the coexisting surface coverage $\theta(t)$.

3. The control system. Cost functionals and the optimal control problem

Since it is assumed that the overpotential evolution $\eta(.)$ can be (within reasonable bounds) manipulated, then it will be the natural *input* or *control* variable for the system Σ under study. On the contrary, the variable θ cannot be directly handled from outside. Once $\eta(.)$ is chosen and applied for $t \leqslant \tau$, then the value of $\theta(\tau)$ contains all the information needed to predict the (near) future evolution of the system, so θ is the natural *state* variable for Σ. The obvious smoothness of HER equations guarantee that for each piecewise continuously differentiable control trajectory $\{\eta(t), 0 \leqslant t \leqslant t^* \leqslant \infty\}$ and for each initial condition $\theta(0) = \theta_0 \in [0, 1]$, there exists a continuous solution trajectory $\{\theta(t), 0 \leqslant t \leqslant t^*\}$.

Mathematically, not more than piecewise continuous differentiability of the input is needed to ascertain the existence and uniqueness of state trajectories, but in what follows $\eta(.)$ will be assumed to belong to $C^1(0, t^*)$. Under such assumptions $\theta(.)$ will actually be not only continuous on $[0, t^*]$ but also continuously differentiable on $(0, t^*)$.

A *steady state* $(\hat{\theta}, \hat{\eta})$ (sometimes called a *set-point*) will be a pair of values for θ and η such that, if they are simultaneously assumed at some time t, then $\dot{\theta}(t) = g(\hat{\theta}, \hat{\eta}) = 0$ (and Σ will not change until the manipulated variable is moved to an unsteady-state value). The physical situations to be considered in the following sections will ask for control trajectories forcing the system to evolve from one steady-state condition:

$$\{(\theta(t), \eta(t)) = (\theta_0, \eta_0^-),\ t < 0\} \quad \text{with}$$
$$g(\theta_0, \eta_0^-) = 0; \quad \text{into another steady-state,}$$

$$\{(\theta(t), \eta(t)) = (\theta_1, \eta_1^+),\ t \geqslant t^*\} \quad \text{with}$$
$$g(\theta_1, \eta_1^+) = 0; \quad \text{through an admissible control path.}$$

The notations $\eta_0 \triangleq \eta(0)$ and $\eta_1 \triangleq \lim_{t \to t^{*-}} \eta(t)$ are used when necessary to allow that $\eta_0 \neq \eta_0^-$ and/or $\eta_1 \neq \eta_1^+$, i.e. that the manipulated variable may jump at the initial and/or final time instants.

Although knowledge of the state $\theta(t)$ is enough to describe the dynamics of Σ, θ-values might not be continuously measured nor registered. The appropriate variable to be observed is the current density J, which in general is a known function $J = h(\theta, \eta)$. If values of J are continuously available, then J is called the *output* of the system Σ. Nonlinear observers for a vast kind of nonlinear systems (Isidori, 1989; García, 1993) have been devised to recuperate the value of the state from input–output information when necessary.

Optimality criteria are often present when searching for control strategies that drive the system from one set-point to another. Usually the input $\eta(.)$ is required to minimize some global cost associated with the set-point change operation. This cost often takes the form of an *objective functional* $\mathscr{J}$ of the form

$$\mathscr{J}(\eta) = \int_0^{t^*} \mathscr{L}(\theta(t), \eta(t))\,\mathrm{d}t + \mathscr{K}(\theta(t^*)),$$

where $\mathscr{L}$ is called the *Lagrangian* of the optimal control problem, and $\mathscr{K}$ is some final penalty, eventually null. Finite or infinite horizons t^* give rise to different optimal control problems. Infinite horizon problems are more likely to accept state-feedback solutions than finite horizon situations. In this paper both kinds of problems will be treated.

4. Continuous piecewise-differentiable overpotential operation. The RC-circuit approximation

In some process control applications, manipulated variables cannot be varied abruptly. Even, when changes in set-points are to be performed, it may be desirable to split the process into a series of smaller changes due to uncertainties in the dynamics when the system is subject to big perturbations. This is equivalent in the limit to restrict the set of admissible control trajectories to some reasonably smooth functions. In this section, nearly local situations will be considered, which means that some locally accurate approximation of the dynamics may be practical in conjunction with continuous, piecewise differentiable, control functions.

Different physical analogical approximations have been proposed for the HER mechanisms, or for the behavior of the system in some regions of the space of parameters (see for instance Harrington and Conway (1987), and the references therein; Vincent and Scrosati, 1997). Here a two-branches in parallel *RC*-electrical circuit simile will be considered, its dynamics condensed in the equation

$$I = \frac{\eta}{R} + C\dot{\eta}, \tag{5}$$

where I is the total current intensity in the circuit (associated to the current HERs density J by the analogy $J \simeq I/A$, where A is the area of the electrode surface). I is modelled as the sum of η/R the current flowing through the "pure resistance" branch having virtual resistance R, and $C\dot{\eta}$ is the current on the other branch having adsorption pseudocapacitance C (usually assigned to the cumulative effect of the hydrogen ions adsorbed in layers over the electrode surface). η the (over) voltage applied to the whole system.

The optimization problem posed is to "find the smooth trajectory $\eta(.)$ that minimizes the cost functional

$$\mathscr{J}_{RC}(\eta) = \int_0^{t^*} (P(t) - P_0)^2\, \mathrm{d}t, \tag{6}$$

where $P(t) \triangleq I(t)\eta(t)$ is the electrical power being consumed during the set-point-change operation

$$\eta(t \leqslant 0) = \eta_0 = \eta_0^-, \quad \eta(t \geqslant t^*) = \eta_1 = \eta_1^+, \tag{7}$$

$$I(t \leqslant 0) = I_0 = \frac{\eta_0}{R}, \quad I(t \geqslant t^*) = I_1 = \frac{\eta_1}{R} \tag{8}$$

and $P_0 \triangleq P(0) = I_0\eta_0 = \eta_0^2/R$, allowing $\eta(.)$ to be just continuous at the initial and final times".

This is an optimization problem in the context of the Calculus of Variations (Gelfand and Fomin, 1963). The Lagrangian function, equivalent to the "trajectory cost" in optimal control terminology, is in this case

$$L(\eta, \dot{\eta}) \triangleq (P - P_0)^2 = \left(\frac{\eta^2}{R} + C\eta\dot{\eta} - P_0\right)^2. \tag{9}$$

The optimal solution $\tilde{\eta}(.)$ is sought amongst the curves that: (i) are smooth in $(0, t^*)$, and (ii) remain continuous at both ends of the time-interval, where they assume the required values η_0 and η_1. Under these conditions it is well known that $\tilde{\eta}(.)$ should satisfy the second-order Euler–Lagrange equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{\eta}}\right) = \frac{\partial L}{\partial \eta} \tag{10}$$

which in this (autonomous) case reduces to the following first-order ODE:

$$L - \dot{\eta}\frac{\partial L}{\partial \dot{\eta}} = K \quad \text{(integration constant).} \tag{11}$$

After some algebraic manipulation the square $\tilde{\mu} \triangleq \tilde{\eta}^2$ of the optimal solution can be found analytically:

$$\tilde{\mu}(t) = \mu_0 + \frac{1}{2}(\gamma(t) - 1)\sqrt{\frac{c - \mu_0^2}{\gamma(t)}}, \tag{12}$$

where $\gamma(t) \triangleq \mathrm{e}^{4t/RC}$, $\gamma^* \triangleq \gamma(t^*)$, $\mu^* \triangleq \mu(t^*)$ and then the relationships between boundary conditions and integration constants can be made explicit:

$$c \triangleq \frac{(1+\gamma^*)^2\mu_0^2 - 8\gamma^*\mu_0\mu^* + 4\gamma^*\mu^{*2}}{(\gamma^* - 1)^2}, \tag{13}$$

$$K = \frac{\mu_0^2 - c}{R^2} \tag{14}$$

and the optimal cost can also be calculated in terms of the parameters of the problem

$$\mathscr{J}_{RC}(\tilde{\eta}) = \frac{RC}{4}K(1 - \gamma^*). \tag{15}$$

An illustration of these results, showing also the minimality of the cost with respect to a family of parabolic trajectories (depending on a perturbation parameter epsilon) is shown in Figs. 2 and 3. The (arbitrary) boundary conditions

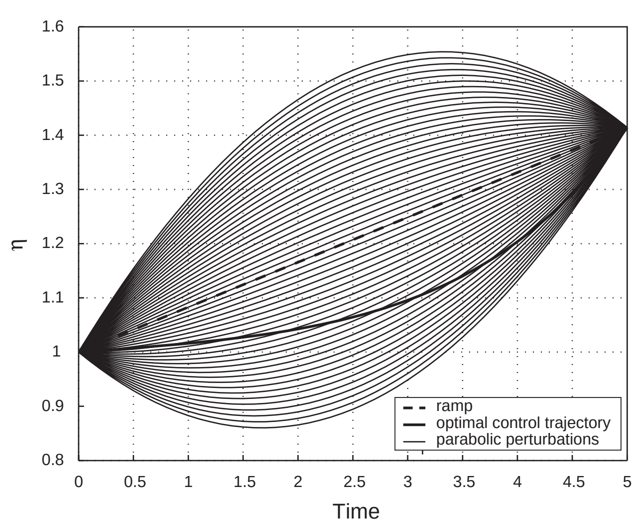

Fig. 2. Optimal trajectory and parabolic perturbations.

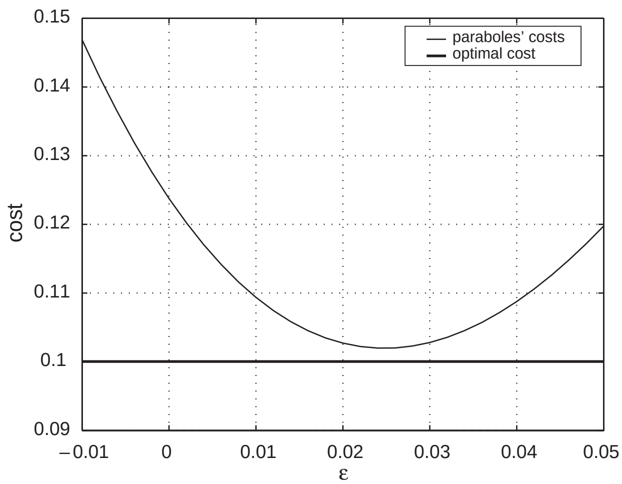

Fig. 3. Optimal and perturbations' costs.

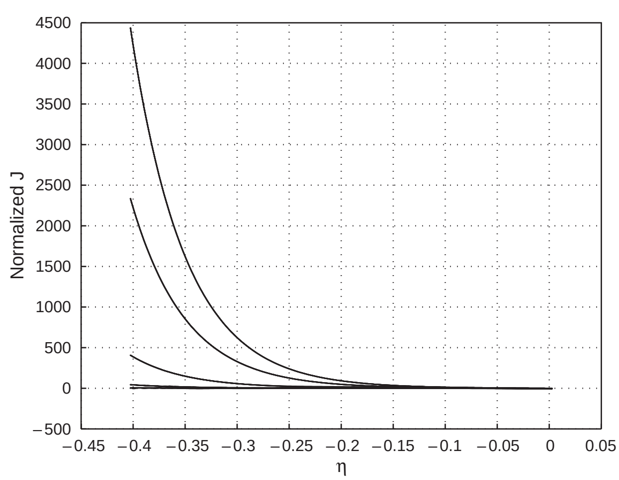

Fig. 4. Normalized current density vs. overpotential (parameter values as in Fig. 1).

and parameters' values used in this illustration are $\mu_0 = 1$, $\mu_1 = 2$, $R = 5$, $C = 0.5$. The straight line in Fig. 2 is just one member of the family of parabolic perturbations.

Despite the advantage of counting with an analytical solution to this problem, the validity of the *RC*-approximation is limited to nearly local applications. For instance, returning to the simulation of the system's response to sawtooth-like periodic forcing, the failure of the *RC*-model to describe global behavior can be seen in Fig. 4. Since $\dot{\eta}(.)$ is piecewise constant for each curve, then the current density $J(.)$ (in the *RC*-case proportional to the current intensity $I(.)$), should look as a straight line function of η, which is approximately true only locally.

5. Piecewise-continuous control

When local approximations are not sufficiently accurate, or when changing of set-points imply significant variations in the state variable, then the full nonlinearity of the system should be handled. Consequently, the original dynamics 4 will be considered in this section, together with the observation function

$$J = F(v_V + v_H)\left(\triangleq h(\theta, \eta)\right) \tag{16}$$

and the associated "power density" $\mathscr{P}$, defined by

$$\mathscr{P}(t) \triangleq J(t)\eta(t). \tag{17}$$

The generalized cost objective will allow for a balance between "power spending" and "state accuracy", namely

$$\mathscr{J}(\eta) = \int_0^{t^*} \left[r(\mathscr{P}(t) - \mathscr{P}_0)^2 + (\theta - \theta_1)^2\right] \mathrm{d}t, \tag{18}$$

where the value of the "weight parameter" r is left to the designer's. Notice that despite its appearance the Lagrangian is not classically quadratic (the sum of two quadratic terms, one on η and the other one on θ), since the power $\mathscr{P}(t)$ implies a product between the control and the state variables. Minimizing the partial cost $(\mathscr{P}(t) - \mathscr{P}_0)^2$ would imply to maintain the power variable as close as possible to the original one. Since there is not a final penalty $\mathscr{K}(\theta_1)$ involved here, it turns necessary to make explicit the "need to reach θ_1" inside the Lagrangian, and this is the meaning of the partial cost $(\theta - \theta_1)^2$. The introduction of this term has the collateral benefit of precluding the trivial solution "$\mathscr{P}(t) = \mathscr{P}_0\ \forall t$". When adopting r, the orders of magnitude and the different physical units of both antagonistic terms in the Lagrangian should be taken into account.

It is important to notice that, since $\mathscr{J}(\eta) = \int_0^{t^*} \left\{r[h(\theta(t), \eta(t))\eta(t) - \mathscr{P}_0]^2 + (\theta - \theta_1)^2\right\} \mathrm{d}t = \int_0^{t^*} \mathscr{L}(\theta(t), \eta(t))\,\mathrm{d}t$, then the Lagrangian does not explicitly depend on the "speed" $\dot{\eta}(t)$ of the control trajectory, as it was the case in the *RC*-approximation 9; and that $\theta(t)$ appears as a new variable, not directly expressible in terms of $\eta(t)$ nor $\dot{\eta}(t)$. These facts already indicate that a solution through the Euler–Lagrange equation is not straightforward.

Besides, in Section 4 it was not fully exploited the "manipulated" character of the variable η, since it was forced to be strictly continuous as a function of time (especially at the initial and final times). Now the control will be allowed to have discontinuities at the boundary of the time interval. In fact, in the example worked out below, $\eta(0)$ and $\eta(t^*)$ turn out to differ from the steady-state (constraint) values $\eta_0^- = \eta(t < 0)$, and $\eta_1^+ = \eta(t > t^*)$, respectively.

But, if the implicit function theorem can be applied to the dynamics (4) (if $\partial g/\partial\eta$ is nonzero in a sufficiently open subset of phase-space), then η can be regarded as a function of the two variables θ and $\dot{\theta}$, say $\eta \triangleq k(\theta, \dot{\theta})$. Moreover, under the current smoothness assumptions, the relevant partial derivative D_2k can be obtained from the function $g(\theta, \eta)$, which is part of the data

$$\frac{\partial \eta}{\partial \dot{\theta}}(\theta, \dot{\theta}) = D_2 k(\theta, \dot{\theta}) = \frac{1}{D_2 g(\theta, k(\theta, \dot{\theta}))} = \left[\frac{\partial g}{\partial \eta}(\theta, \eta)\right]^{-1}. \quad (19)$$

Therefore, to explore the calculus of variation suitability to the problem at hand, the following change of variables is dictated

$$(\theta, \eta) \to (\theta, \dot{\theta}). \quad (20)$$

In these new variables the Lagrangian function would formally read

$$L(\theta, \dot{\theta}) = \mathscr{L}(\theta, k(\theta, \dot{\theta})) = \mathscr{L}(\theta, \eta) \quad (21)$$

and then the optimal control problem would be appropriately rephrased as to minimize the cost functional

$$\mathscr{J}_{\text{new}}(\theta) = \int_0^{t^*} L(\theta(t), \dot{\theta}(t))\, \mathrm{d}t = \mathscr{J}(\eta) \quad (22)$$

amongst all the admissible (continuous, piecewise differentiable) state trajectories $\theta(.)$, which correspond in a one-to-one way to the admissible piecewise-differentiable control strategies $\eta(.)$ through the solution of the dynamics equation, and that meet classical boundary conditions at the time ends: $\theta(0) = \theta_0, \theta(t^*) = \theta_1$.

Since the new L is again autonomous, then the first integral of the Euler equation $L - \dot{\theta} L_{\dot{\theta}} = K$ will be valid for such optimal state trajectory, at least in the interior of the time interval. The data constrains on η outside this domain are useful to determine the starting and final values of the state variable θ through:

(i) $\eta(t < 0) = \eta_0^-$ implies that $\theta(t \leqslant 0) = \theta_0 = \theta_{\text{equil}}(\eta_0^-)$,
(ii) $\eta(t > 0) = \eta_1^+$ implies that $\theta(t \leqslant t^*) = \theta_1 = \theta_{\text{equil}}(\eta_1^+)$, where $\theta_{\text{equil}}(\eta)$ denotes the only physically meaningful solution for θ to the equation $g(\theta, \eta) = 0$, namely

$$\theta_{\text{equil}}(\eta) = \frac{1}{4(v_T^e)(2\theta_e - 1)} \times \left\{ 4v_T^e \theta_e^2 + v_V^e \theta_e (1 - \theta_e) \left[\hat{E} + (\check{E} - \hat{E})\theta_e\right] + \check{E} v_H^e \theta_e (1 - \theta_e)\left[1 + (\bar{E} - 1)\theta_e\right] - \theta_e \sqrt{\begin{array}{l} 4v_T^e(2-4\theta_e)\left[2v_T^e + (1-\theta_e)(\hat{E}v_H^e + \check{E}v_V^e)\right] \\ + \left\{4v_T^e\theta_e + v_V^e(1-\theta_e)\left[\hat{E} + (\check{E}-\hat{E})\theta_e\right] \\ + \check{E}v_H^e(1-\theta_e)\left[1 + (\bar{E} - 1)\theta_e\right]\right\}^2 \end{array}} \right\},$$

where for simplicity, the following notations were used $\bar{E} \triangleq \mathrm{e}^{f\eta}$, $\hat{E} \triangleq \mathrm{e}^{\alpha f \eta}$, $\check{E} \triangleq \mathrm{e}^{(\alpha - 1) f \eta}$.

Since in calculating the partial derivative $L_{\dot{\theta}}$ the variable θ is kept constant, then Euler's equation can finally be written

$$L - \dot{\theta} L_{\dot{\theta}} = \mathscr{L} - g \mathscr{L}_\eta \frac{\partial \eta}{\partial \dot{\theta}} = \mathscr{L} - g \frac{\partial \mathscr{L}/\partial \eta}{\partial g / \partial \eta} = m(\theta, \eta) = K \quad (23)$$

which, since

$$\frac{\partial g}{\partial \eta} \neq 0 \Longrightarrow \frac{\partial m}{\partial \eta} \neq 0, \quad (24)$$

then by the implicit function theorem the existence of an optimal feedback control law

$$\eta = u_K(\theta) \text{ such that } m(\theta, u_K(\theta)) = K \ \forall \theta \text{ between } \theta_0 \text{ and } \theta_1 \quad (25)$$

is guaranteed.

The function $m(\theta, \eta)$ plays the role of a Hamiltonian for the optimal control system, since it is constant along each optimal trajectory. Some additional information can be obtained from the Hamiltonian formalism, as will be evident in Section 7. Unfortunately, this constant value K is unknown for the desired trajectory ending exactly at $\theta(t^*) = \theta_1$. However, usually a good approximation can be obtained from

$$K \approx K_\infty = \lim_{t^* \to \infty} K(t^*) = r(\mathscr{P}_1 - \mathscr{P}_0)^2 \quad (26)$$

since using $\eta = u_{K_\infty}(\theta)$, by continuity of solutions on parameters, the variables must converge to the target set-point as $t \to \infty$, i.e.

$$\eta \to \eta_1^+, \quad \theta \to \theta_1, \quad \dot{\theta} = g(\theta, \eta) \to g(\theta_1, \eta_1^+) = 0,$$
$$\mathscr{P} \to \mathscr{P}_1 \triangleq h(\theta_1, \eta_1^+)\eta_1^+. \quad (27)$$

Moreover, the analytical expression of the feedback law $u_{K_\infty}(\theta)$ is not necessary for calculations, nor its repeated numerical evaluation as the root of the nonlinear algebraic Eq. (25). In fact, if $\theta_{\text{opt}}(.)$ is the optimal state trajectory corresponding to the optimal control trajectory $\eta_{\text{opt}}(.) = u_{K_\infty}(\theta_{\text{opt}}(.))$, and by calling $M(t) \triangleq m(\theta_{\text{opt}}(t), \eta_{\text{opt}}(t)), t \in [0, t^*]$, then the Hamiltonian property of m will require that, in the whole time interval,

$$\dot{M} = \frac{\partial m}{\partial \theta} \dot{\theta}_{\text{opt}} + \frac{\partial m}{\partial \eta} \dot{\eta}_{\text{opt}} = 0. \quad (28)$$

Therefore the pair $(\theta_{\text{opt}}(.), \eta_{\text{opt}}(.))$ can be obtained as the solution to the pair of coupled nonlinear ODEs

$$\dot{\theta} = g(\theta, \eta), \quad \theta(0) = \theta_0, \quad (29a)$$

$$\dot{\eta} = -\frac{(\partial m/\partial \theta)(\theta, \eta)}{(\partial m/\partial \eta)(\theta, \eta)} g(\theta, \eta), \quad \eta(0) = \eta_0^+ \triangleq u_{K_\infty}(\theta_0), \quad (29b)$$

where it is clear that just one evaluation of u_{K_∞} is needed, namely $u_{K_\infty}(\theta_0)$.

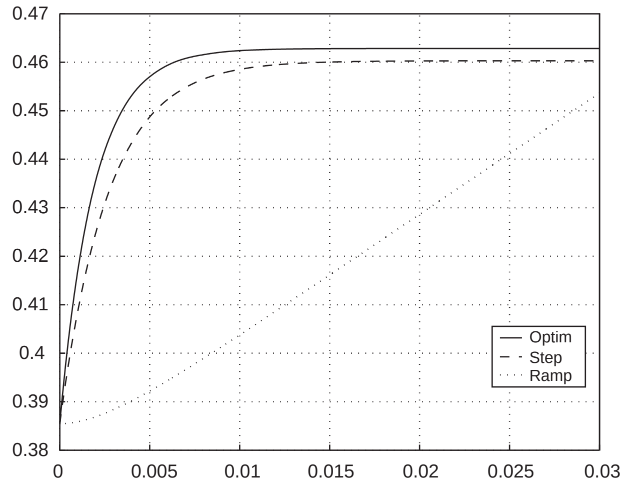

Fig. 5. Theta(t).

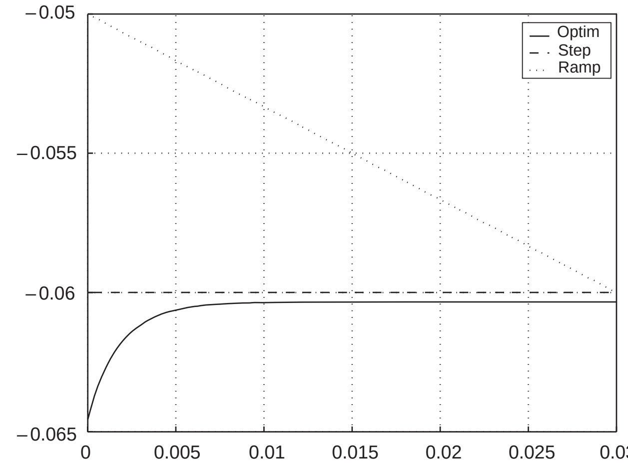

Fig. 6. Eta(t).

Putting these results together, the proposed strategy for the set-point change operation would consist of the following steps:

- adopt a value for the weight factor r;
- evaluate $K_\infty = r\left[h(\theta_1, \eta_1^+)\eta_1^+ - h(\theta_0, \eta_0^-)\eta_0^-\right]^2$;
- determine (numerically if necessary) the initial control value η_0^+, as the root of $m(\theta_0, \eta_0^+) = K_\infty$;
- start the control at $t = 0$, imposing a "jump" in the over-potential $\eta_0^- \to \eta_0^+$;
- solve (numerically) Eqs. (29a) and (29b) for $t > 0$. The resulting control $\eta_{\text{opt}}(.)$ will asymptotically drive the state to the desired value θ_1, but to better conform to time constrains;
- at time t^* (if $t^* < \infty$) impose the final jump $\eta_1^- \triangleq \eta(t^*) \to \eta_1^+$ to the manipulated variable, and keep this value constant for $t > t^*$.

An example with the main boundary restrictions:

$$\eta_0^- = -0.05, \quad \eta_1^+ = -0.06$$

and the parameter values $v_T^e = 10^{-9}$, $v_H^e = 10^{-10}$ and $v_V^e = 10^{-7}$ was worked out, and the results are illustrated in Figs. 5–7.

A value of $r = 10^4$ was adopted, giving some preeminence to the contribution of the term $(\theta - \theta_1)^2 = \mathcal{O}(10^{-3})$ over the term $(\mathcal{P}_\infty - \mathcal{P}_0)^2 = \mathcal{O}(10^{-8})$ in the definition of the total cost. The following calculations were performed off-line:

$$\theta_0 = \theta_{\text{equil}}(\eta_0^-) = 0.3855,$$

$$\theta_1 = \theta_{\text{equil}}(\eta_1^+) = 0.4603,$$

$$J_0^- \triangleq h(\theta_0, \eta_0^-) = 0.002966,$$

$$J_\infty \triangleq h(\theta_1, \eta_1^+) = 0.004296,$$

$$\mathcal{P}_0 \triangleq J_0^- \eta_0^- = -0.0001483,$$

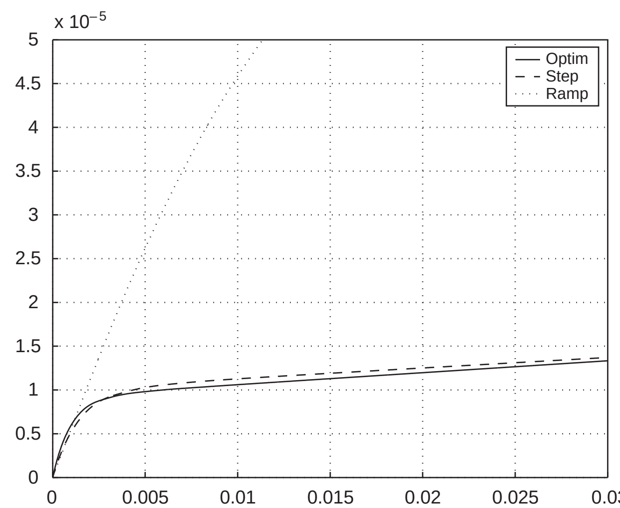

Fig. 7. Cost(t).

$$\mathcal{P}_\infty \triangleq J_\infty \eta_1^+ = -0.0002578,$$

$$K_\infty \triangleq r(\mathcal{P}_\infty - \mathcal{P}_0)^2 = 1.199 \times 10^{-4},$$

$$\eta_0^+ \triangleq (\text{root of } m(\theta_0, \eta) = K_\infty) \approx -0.06456,$$

$$J_0^+ \triangleq h(\theta_0, \eta_0^+) = 1.1985 \times 10^{-2},$$

$$\mathcal{P}_0^+ \triangleq J_0^+ \eta_0^+ = -7.7372 \times 10^{-4},$$

$$J_{0_{\text{step}}}^+ \triangleq h(\theta_0, \eta_{0_{\text{step}}}^+) = h(\theta_0, \eta_1^+) = 0.9093 \times 10^{-2},$$

$$\mathcal{P}_{0_{\text{step}}}^+ \triangleq J_{0_{\text{step}}}^+ \eta_{0_{\text{step}}}^+ = J_{0_{\text{step}}}^+ \eta_1^+ = -5.4560 \times 10^{-4}.$$

Notice that η_0^+ results smaller than η_1^+, which implies $|\eta_0^- - \eta_0^+| > |\eta_0^- - \eta_1^+|$. In other words, at the initial time the optimal control requires a bigger jump in η, than if applying a "blind" step change from the original steady value η_0^- to the desired final value η_1^+. A bigger initial jump costs more in electrical power units since

$$|\mathscr{P}_0^+ - \mathscr{P}_0| > |\mathscr{P}_{0_{\text{step}}}^+ - \mathscr{P}_0|$$

and this expense begins to dominate the cost, as reflected in the first part of the cost trajectories. But the optimal control jump drives the state nearer to the desired value θ_1, which after some time compensates for the initial control effort. After this compensation the term $(\theta - \theta_1)^2$ begins to dominate the total cost, and then in advance the optimal trajectory has a smaller cost than the step function response (see Fig. 7). At the end the difference in cost is not significative in this case because the value chosen for r assigns little relative weight to electrical power expenditures. If the value of r is decreased, then the optimal control will expend less power at the beginning (because it would cost more), and then the savings with respect to the step control cost would increase. Also this difference in costs could vary with boundary conditions and with the time duration of the process.

A comparison against the performance of a continuous linear growth (ramp) of the manipulated variable is also included to show that the choice of piecewise continuous strategies as the set of admissible control functions is remarkably profitable.

6. The phase-space for optimal trajectories

The numerical solution to the optimal control problem posed in Section 5, for an infinite time-horizon ($K = K_\infty$), is translated to the phase-space (θ, η) in Figs. 8 and 9. The exact optimal solution should asymptotically approach the equilibrium (θ_1, η_1^+), so the numerical approach seems fairly accurate. These results suggest that a practical stopping time t_δ could be decided during operation ($t_\delta \leqslant t^*$), for instance if some prescribed tolerance δ is reached: $|\theta(t_\delta) - \theta_1| < \delta$.

The locus of equilibrium points $(\theta_{\text{equil}}(\eta), \eta)$ for the original dynamics ($\dot{\theta} = g = 0$) is also plotted in Fig. 9, together with the set of points for which $\partial m/\partial\theta = 0$, i.e. $\dot{\eta} = 0$ (see Eq. (29b)). The intersection of these two loci is (θ_1, η_1^+), which is an isolated fixed point for the coupled ODEs in (θ, η) discussed before. Clearly (θ_1, η_1^+) belongs to the first locus because, by construction, $\theta_1 = \theta_{\text{equil}}(\eta_1^+)$; and to the second one because the term $(\theta - \theta_1)^2$ included in the Lagrangian produces factors $(\theta - \theta_1)$ in the summands of $\partial m/\partial\theta$.

The flow of all optimal trajectories corresponding to different values of K is the family of solutions to the coupled Eqs. (29a) and (29b) with initial conditions $(\theta(0), u_K(\theta(0)))$ (see Fig. 8). Some qualitative features of the level curves have practical value when designing control strategies. For instance, the fixed point looks like a saddle, which implies it is unstable with respect to perturbations in K. Therefore, it seems convenient to always force the manipulated variable to adopt the final desired value η_1^+ after some finite time, even when the time-horizon of the problem was chosen to be infinite. The second observation concerns the periodic orbits enclosed at the right of the fixed point, a typical nonlinear bistability situation. This region, full of trajectories with negative values for K, should be avoided since they could not leave the $K = 0$ boundary to reach the $\dot{\theta} = 0$ locus of

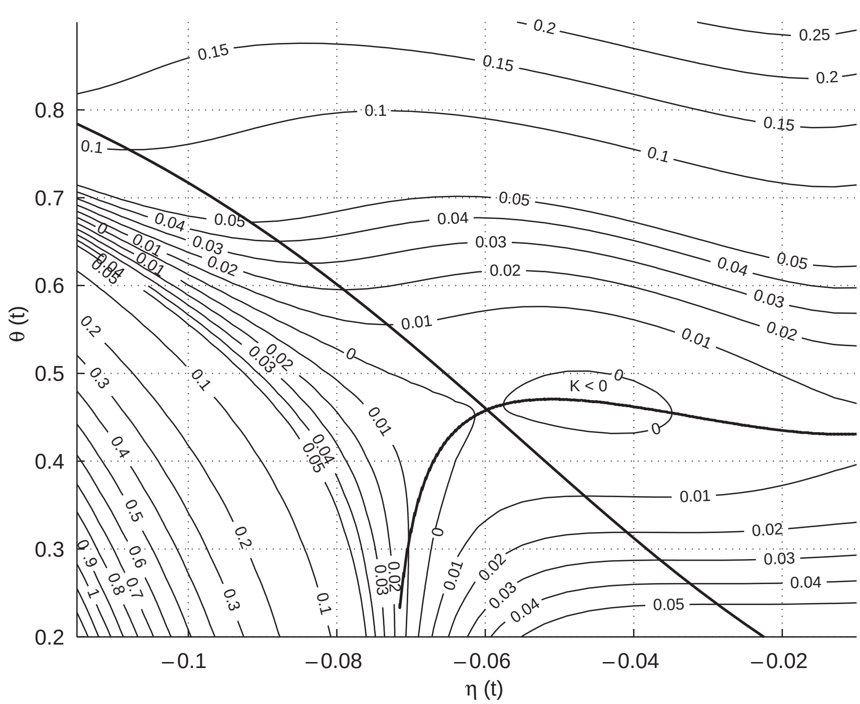

Fig. 8. Level m-curves.

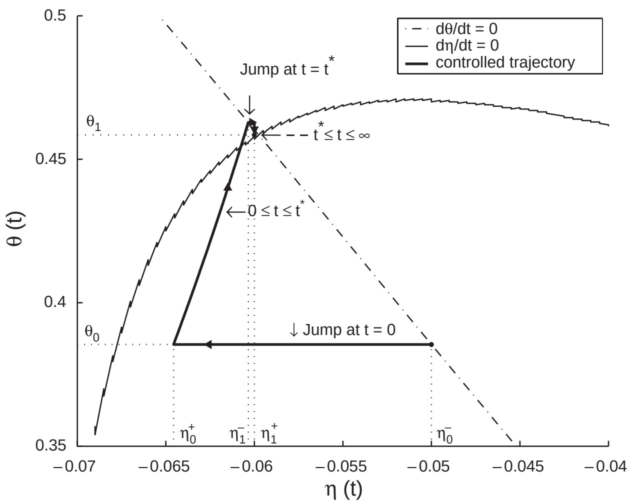

Fig. 9. Optimal trajectory in phase-space.

admissible set-points without additional control action. Other trajectories corresponding to negative K-values should also be discarded, since they do not cross the equilibrium curve but eventually increase their deviation from the target short after crossing the locus of $\dot{\eta} = 0$.

From these observations it seems convenient to generate a plot of the K-level curves for each particular set-point change operation. It would clearly help in designing the treatment of perturbations or unexpected systematic departures from the optimal strategy (Fig. 8).

7. The adjoint variable. Finite-horizon treatment

Still another theoretical aspect of the optimal control set-up will be explored in this section, searching for a closed answer to the finite time-horizon question. A new change of variables $(\theta, \eta) \rightarrow (\theta, \lambda)$, with λ defined by

$$\lambda \triangleq -\frac{\partial \mathscr{L}/\partial \eta}{\partial g/\partial \eta} = -\frac{\partial L}{\partial \dot{\theta}} \tag{30}$$

makes clear the Hamiltonian character of the optimal control problem at hand. Consistently with previous assumptions, from Eq. (23) the variable η can be expressed as a function $\eta^0(\theta, \lambda)$; and after updating old functions to new variables

$$\hat{g}(\theta, \lambda) \triangleq g\left(\theta, \eta^0(\theta, \lambda)\right),$$

$$\hat{L}(\theta, \lambda) \triangleq \mathscr{L}\left(\theta, \eta^0(\theta, \lambda)\right),$$

$$H(\theta, \lambda) \triangleq \hat{L}(\theta, \lambda) + \lambda\, \hat{g}(\theta, \lambda), \tag{31}$$

then the following identities can be easily found (via the "chain rule" and the identity $\partial\mathscr{L}/\partial\eta + \lambda \partial g/\partial \eta = 0$)

$$\frac{\partial H}{\partial \lambda}(\theta, \lambda) = \hat{g}(\theta, \lambda) = g\left(\theta, \eta^0(\theta, \lambda)\right) = \dot{\theta}, \tag{32a}$$

$$\frac{\partial H}{\partial \theta}(\theta, \lambda) = \frac{\partial \mathscr{L}}{\partial \theta}\left(\theta, \eta^0(\theta, \lambda)\right) + \lambda \frac{\partial g}{\partial \theta}\left(\theta, \eta^0(\theta, \lambda)\right). \tag{32b}$$

Since $H(\theta, \lambda) = \mathscr{L}\left(\theta, \eta^0(\theta, \lambda)\right) + \lambda g\left(\theta, \eta^0(\theta, \lambda)\right) = m\left(\theta, \eta^0(\theta, \lambda)\right)$, then, along optimal trajectories

$$\dot{m} = 0 \Longrightarrow \dot{H} = 0 \tag{33}$$

which after additional algebraic manipulations gives

$$\dot{\lambda} = -\frac{\partial \mathscr{L}}{\partial \theta}\left(\theta, \eta^0(\theta, \lambda)\right) - \lambda \frac{\partial g}{\partial \theta}(\theta, \eta^0(\theta, \lambda)) = -\frac{\partial H}{\partial \theta}(\theta, \lambda). \tag{34}$$

Eqs. (32a) and (34) show a Hamiltonian dynamical system in canonical form, with Hamiltonian function $H(\theta, \lambda)$. Besides confirming that the constants K appearing in previous sections have the theoretical meaning of a "first integral" or a "total energy" conserved along trajectories, this formalism allows to obtain some collateral practical results. For instance, supposing the trajectory $(\theta(t), \eta(t))$ is being calculated numerically, then the following functions:

$$\mathscr{L}_\theta(t) \triangleq -\frac{\partial \mathscr{L}}{\partial \theta}(\theta(t), \eta(t)),$$

$$g_\theta(t) \triangleq -\frac{\partial g}{\partial \theta}(\theta(t), \eta(t)) \tag{35}$$

can also be evaluated at each integration time t, and therefore $\lambda(t)$ can be obtained by integrating in parallel the time-dependent linear ODE

$$\dot{\lambda} = \mathscr{L}_\theta(t) - \lambda g_\theta(t). \tag{36}$$

In case K is known, after combining Eqs. (23) and (30), the appropriate initial condition is found, namely

$$\lambda(0) = \frac{K - \mathscr{L}(\theta_0, \eta_0^+)}{g(\theta_0, \eta_0^+)}. \tag{37}$$

The variable λ results then equivalent to the *costate*, or *adjoint variable* (see Kalman et al., 1969) of the Hamiltonian formalism used in optimal control theory. The adjoint plays the role of a generalized Lagrange multiplier, as observed in Eq. (31). It is well known that this generalized multiplier coincides with the gradient

$$\lambda(t) = \frac{\partial V}{\partial \theta}\left(t, \tilde{\theta}(t)\right) \tag{38}$$

of the "*value function*" V of the optimal control problem (also called the "*Bellman function*"), evaluated along the optimal trajectory. The value function V is usually defined in terms of the cost functional, namely

$$V(\tau, \theta_\tau) \triangleq \inf_{\eta(.)} \mathscr{J}_{\theta_\tau}(\eta) = \inf_{\eta(.)} \int_\tau^{t^*} \mathscr{L}\left(\theta(t), \eta(t)\right) \mathrm{d}t, \tag{39}$$

i.e. that $V(\tau, \theta_\tau)$ is the total cost associated to the optimal trajectory that starts at time τ from the state θ_τ. Then, in particular for $\tau=0$, the initial value $\lambda(0)=(\partial V/\partial\theta)(0, \theta_0)$ is approximately equal to the variation of the (optimal) cost due to an unitary increase in the initial state condition, which is the so-called "*marginal cost*" in Economics. Therefore, knowledge of the costate λ may help to take "economical" decisions when considering the magnitude of eventual changes in set-point for the state θ.

When the value of K is not precisely known, then an alternative method for treating the finite-horizon problem can be devised, by using the gradient property of the costate 38 and the absence of a final penalty cost ($\mathscr{K}(\theta)=0\ \forall\theta$), i.e.

$$\lambda(t^*)=\frac{\partial V}{\partial\theta}\left(t^*, \tilde{\theta}(t^*)\right)=\frac{\partial V}{\partial\theta}(t^*, \theta_1)=\frac{\mathrm{d}\mathscr{K}}{\mathrm{d}\theta}(\theta_1)=0. \quad (40)$$

The optimal state $\tilde{\theta}(.)$ and costate $\tilde{\lambda}(.)$ of the finite-horizon problem would then have to satisfy the coupled nonlinear system with boundary conditions

$$\dot{\theta}=\hat{g}(\theta, \lambda), \quad \theta(0)=\theta_0, \quad (41a)$$

$$\dot{\lambda}=-\frac{\partial\hat{L}}{\partial\theta}(\theta, \lambda)-\lambda\frac{\partial\hat{g}}{\partial\theta}(\theta, \lambda), \quad \lambda(t^*)=0 \quad (41b)$$

which, if solved, would automatically render the optimal control $\tilde{\eta}(t)=\eta^0(\tilde{\theta}(t), \tilde{\lambda}(t))$. The solution procedure is in practice an involved numerical calculus problem. Its discussion exceeds the scope and expectations of this paper.

8. Conclusions

In this paper, the solutions to some optimal control problems posed for hydrogen evolution reaction processes are substantiated and illustrated. The basic mathematical set-up is the Calculus of Variations, closely related to optimal control theory. HER equations are irreducibly nonlinear since their flow presents qualitative features that cannot be globally approximated by linear systems, like hysteresis loops and closed periodic orbits far from equilibrium. The optimization of these processes have increasing practical interest in the light of the energy crisis recurrently appearing in contemporary industrialized world.

Although the treatment of steady-state regulation for these systems is potentially important, the main objective here has been to design the optimal control of set-point changes' transient evolutions. In the cases discussed the dynamics cannot be linearized, since the trajectories depart significantly from equilibrium, and there also may exist isolated periodic orbits and other attractor complicating the smooth navigation from one equilibrium to another.

When the initial and final set-points in question are nearby, then a so-called *RC*-approximation to the dynamics is acceptable. If in addition only continuous controls are admissible, then the optimal control can be found in analytical terms by using Euler's equation, fundamental in the Calculus of Variations. This approach proves to be useful also in solving the global original problem, after applying a change of variables and some algebraic manipulations. As the main result of this work the optimal control problem for piecewise continuous controls is then obtained in the form of an implicit state-feedback law, which can be replaced by the on-line integration of a differential equation for the overpotential variable.

In finite-horizon situations the proposed strategy results suboptimal, though accurate enough for engineering purposes. The basic equations for an alternative treatment of finite-time restrictions based on the Hamiltonian formalism are presented but not applied to the present problem due to its numerical involvement.

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