A Model for Stimulated and Co-operative Electron Transfer

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1. Introduction

The paradigm of self-organization plays an increasing role in the attempts of reunification of sciences. Due to Prigogine´s fundamental work the old paradox of emergence of highly complex order in living systems on the one hand, and the increase of entropy demanded by the second law of thermodynamics on the other hand, was resolved. Therefore one is tempted to say that the modern biology must be the very natural field of self-organization theory. This is, indeed, the case in population dynamics, in the theory of emergence of life (Eigen´s Hypercycle) and in some special oscillating biochemical reactions.

But, surprisingly, in other parts of biology and biochemistry, e.g. in bioenergetics or in the speciation theory (the so called synthetic theory of evolution), the ideas of self-organization today are rather not applied. On the contrary, we know that all living organisms and so all of it's subunits like cells or macromolecules are thermodynamically open systems, able to self-organized structuring of the intrinsic chemical and electrochemical processes. Therefore it is, to our understanding, a useful heuristic approach to develop alternative models which show the possibility that self-organization processes in principle can be used by nature to effectivate the capabilities of living systems (for the speciation theory see[1]).

Some of the most important electrocatalytic mechanisms such as water splitting, carbon dioxide and nitrogen fixation, sulphate and oxygen reduction are multi-electron processes, which only proceed close to the favourable thermodynamic overall potential, when undesirable intermediates are avoided and electrons are transferred more or less simultaneously. These reactions are very successfully handled by biological systems at environmental temperatures, but generate significant difficulties for development in technical processes. Accordingly, the need to consider autocatalytic mechanisms as a way of making photoinduced interfacial

electron transfer more efficient for solar energy conversion has been discussed by one of the authors[2].

Biological systems typically apply multicentre catalysts (e.g. cytochrome oxidase, manganese centre of photosynthesis, cytochrome c_3 of sulphate reducing bacteria) which show significant interactions between their metal centres and probably utilise feedback mechanisms. This indicates the presence of far from equilibrium processes, where the co-operative phenomena of irreversible thermodynamics become possible.

The internal electronic feedback has recently been especially well demonstrated between the four heme groups of cytochrome c_3 of *Desulfovibrio vulgaris*. Whenever an electron is exchanged, all heme groups change to a smaller or larger extent their oxidation state and their internal redox potential.[3] This means that in multi-electron transfer reactions the first electron to be transferred may exert a positive feedback effect on the transfer of the second one and so on (like chemical autocatalysis).

The aim of this paper is to prove on the basis of a simple model that far from equilibrium co-operative electron transfer is indeed possible.

2. Modelling Strategy

Our model was inspired by an idea of Prigogine from 1965[4] concerning a sequence of equivalent chemical reactions in a homogeneous liquid environment with catalytic feedback as a model for the remarkably high reaction efficiency of certain molecular biochemical mechanisms:

$$\begin{array}{l} A \overset{1}{\longleftrightarrow} X_1 \overset{2}{\longleftrightarrow} X_2 \overset{3}{\longleftrightarrow} \ldots X_n \overset{n+1}{\longleftrightarrow} B \\ \qquad\qquad\qquad\qquad\quad \uparrow\downarrow {\scriptstyle n+2} \\ \qquad\qquad\qquad\qquad\quad M \end{array} \qquad (1)$$

with

$$k_1 = k_1' = \ldots = k_n = k_n' = k = 1 + \alpha M$$
$$k_{n+1} = k_{n+1}' = 1 \qquad (2)$$

Here, the substance M is some intermediate, which catalyses the reactions 1 to n in the reaction chain.

Under non-equilibrium conditions (A>>B), but without feedback (α=0) the stationary value of the last intermediate X_n is very small:

$$X_n = B + O(1/n) . \qquad (3a)$$

However, when $\alpha \rightarrow \infty$ (strong feedback):

$$X_n \rightarrow A . \qquad (3b)$$

In this way certain reaction products in biochemical reactions can be, in contrast to classical expectations, produced in high concentrations due to feedback couplings.

We will now try to develop this simple theoretical approach for electron transfer reactions along molecular electron transfer chains in membranes and through interfacial electron transfer complexes, which are involved in multi-step electron transfer processes. For this purpose, first we will interpret Prigogines model as a sequence of electron transfer reactions

$$(X_i + e; X_{i+1}) \leftrightarrow (X_i ; X_{i+1} + e),$$

(i.e. the X_i is interpreted as electron density at the site i) and second we will assume reaction rates, which are not equal for forward and backward reactions, i.e. the ratio

$$\kappa = k/k'$$

is in general not equal to unity. Therefore we obtain a set of non-linear differential equations:

$$\frac{dX_i}{dt} = \beta(kX_{i-1} - k'X_i - kX_i + k'X_{i+1}),\ X_0 = A,\ i = 1,\ldots,\ n-1$$

$$\frac{dX_n}{dt} = \beta(kX_{n-1} - k'X_n) - kX_n + k'B - aX_n + a'M \qquad (4)$$

$$\frac{dM}{dt} = aX_n - a'M$$

with

$$k_1 = \ldots = k_n = k\beta\ ;\quad k'_1 = \ldots = k'_n = k'\beta$$
$$k_{n+1} = k';\ k'_{n+1} = k';\ \kappa = k/k';\ \kappa_a = k_{n+2}/k'_{n+2}\ , \qquad (5)$$

where $\beta = 1 + \alpha\kappa_a X_n$.

3. Analytic and Numerical Solutions: Stimulated Electron Transfer

In the steady state case, the corresponding set of (n+1) algebraic equations can be solved analytically:

$$X_i = \frac{\left[(\beta\kappa - \beta - \kappa)\kappa^i + \kappa^{n+1}\right]A - \left(1 - \kappa^i\right)B}{(\beta\kappa - \beta - \kappa) + \kappa^{n+1}} \quad \text{where } \beta = 1 + \alpha\kappa_a X_n \qquad (6)$$

For κ=1 the results obtained by Prigogine can be obtained for the limiting cases of vanishing and of very strong feedback, respectively.

Furthermore it should be noted that this discrete model can be extended to a model with continuously changing states leading to a kind of non-linear diffusion equation with variable diffusion coefficient and with a migration term.[5] The numerical results obtained by this model are qualitatively similar to the results of the discrete one. For the sake of simplicity we will restrict our considerations here on the discrete model.

For the case of "isotropic" e-transfer kinetics (κ=1) we obtain a result similar to that of Prigogine´s model: With increasing feedback parameter α the electron density at the last

intermediate site also increases up to the maximal value, which cannot exceed the value of the left boundary condition A (Fig.1).

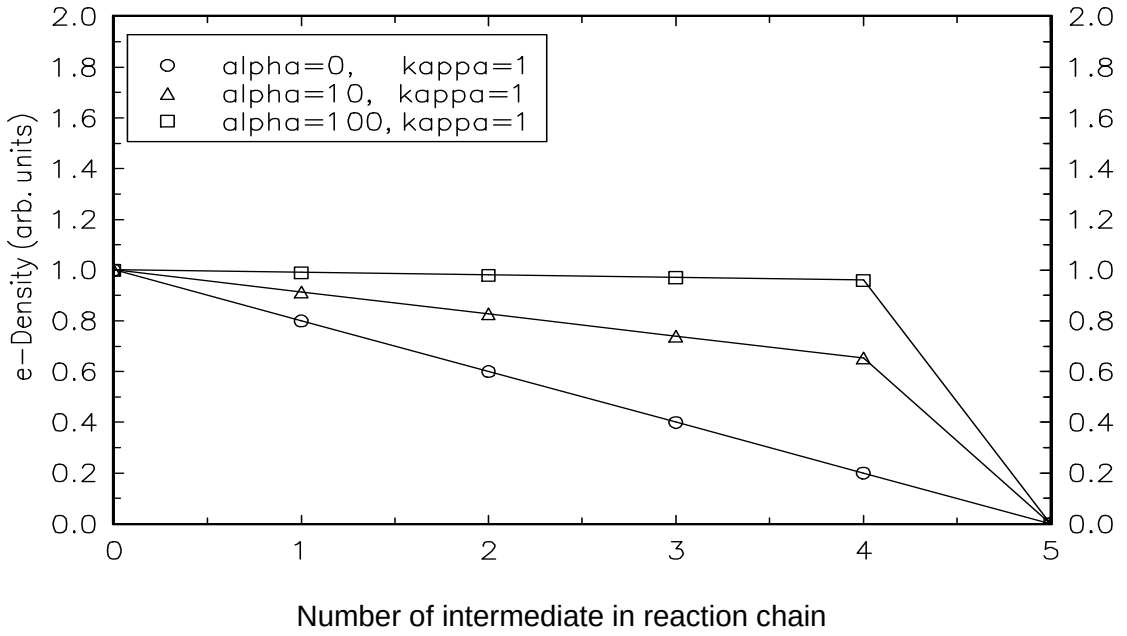

Fig. 1. Electron density along reaction chain for different values of α and isotropic electron transfer ($\kappa = 1$)

On the contrary, in the case of "anisotropic" e-transfer kinetics ($\kappa>1$), an increase of the feedback parameter α causes an increase of the electron densities at the intermediate sites, which are not limited by the value of A. (Mathematically, this is a consequence of the nonlinearity of the equations, which appears only if $\alpha \neq 0$.) Thus, here the feedback increases the value of X_n, and therefore the resulting stationary electron flux, in a dramatic way, which we will call feedback stimulated electron transfer (Fig.2).

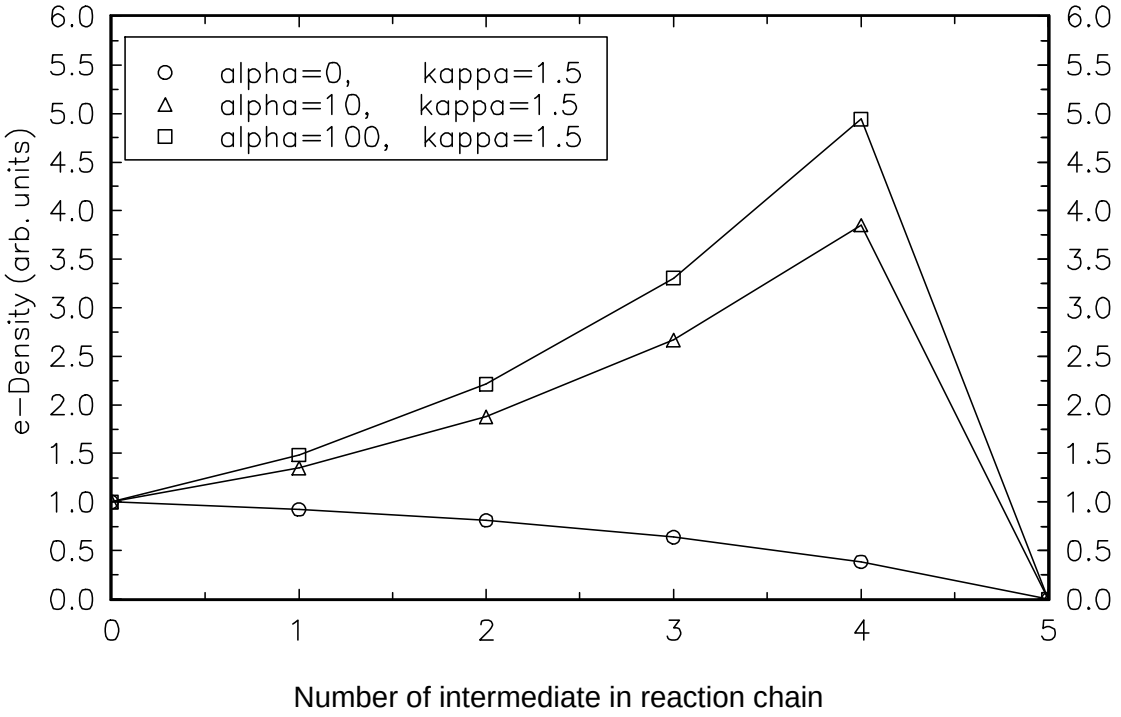

Fig. 2. Electron density along reaction chain for different values of α and anisotropic electron transfer ($\kappa > 1$)

4. Introducing Co-operativity. Order Parameter Equation

The above described model shows the feature of stimulated electron transfer, but co-operative electron transfer could not be demonstrated. Co-operativity we understand in the sense of Haken´s synergetics[6], i.e. when one ore few modes of a system with many degrees of freedom become unstable at a bifurcation point, so all remaining stable modes will be "slaved" in their motion by the motion of these few "order parameters". Therefore, co-operation appears as a drastic reduction of degrees of freedom of the complex system. Haken originally introduced his concept of synergetics for the laser, where the many independently emitting atoms become slaved by one or very few modes of the electromagnetic field. Consequently the atoms will emit in a very co-operative way.

In our model, one can show that an autocatalytic production of the catalytic acting intermediate M, instead of the first order reaction above, leads to co-operative behaviour:

$$M + X_n \underset{\leftarrow}{\overset{\mu}{\rightarrow}} 2M\,; \qquad \frac{dM}{dt} = M(\mu X_n - M) \quad (7)$$

This model also can be solved analytically in the stationary case, which leads to three solutions, one corresponding to $M^{(1)} = 0$ (feedback is switched off):

$$X_{n,1} = \kappa^n/(\kappa^n + \kappa^{n-1} + ... + 1) \quad , \quad (8)$$

the other two corresponding to $M^{(2)} = \mu X_n$ (feedback is switched on):

$$X_{n,2,3} = -(D \pm \sqrt{(D^2 + 4\alpha\mu\kappa^n)})/2\alpha\mu \;, \; D = (\kappa^n + \kappa^{n-1} + ... + 1 - \alpha\mu\kappa^n). \quad (9)$$

Here one solution is always negative and therefore without physical sense. Hence there are two relevant states of the system, i.e. two positive solution branches in the bifurcation diagram with the bifurcation parameter μ. Their intersection at $\mu=0$ is the bifurcation point. To determine the type of stability change at the bifurcation point one must carry out a stability analysis.

The linear stability analysis of the model is based on the linearization of the differential equation system around a stationary state, e.g. around the state $X_{n,1}$. From the corresponding Jacobi matrix $[\partial Fi/\partial Xi]$ we obtain, following the standard procedure, the eigenvalues:

$$\sigma_1 = \mu X_{n,1}$$

$$\sigma_{i+1} = -(1+\kappa) + 2\sqrt{(\kappa \cos A_i)} < 0 \quad (10)$$

$$A_i = i\pi/(n+1), \; i = 1,2,...,n \; .$$

Hence, at $\mu=0$ only one eigenvalue, σ_1, changes its sign and all remaining are smaller than zero. According to the slaving principle, all (n+1) degrees of freedom reduce to only one degree of freedom. The slowest mode, which is just becoming unstable (following Haken, the order parameter, which is in our system M), is slaving all other stable modes. Following the slaving principle (i.e. a kind of adiabatic elimination), it remains only one differential equation describing the evolution of the order parameter: After inserting of the expression for the dependence of $X_n(M)$ on M in the differential equation for M,

$$\frac{dM}{dt} = M(\mu X_n(M) - M), \quad X_n(M) = \frac{\beta(M)\kappa^n}{\kappa^n + \kappa^{n-1} + \ldots + \kappa + \beta(M)} ,$$

$$\beta(M) = 1 + \alpha M$$

we obtain for M a non-linear differential equation of first order

$$\frac{dM}{dt} = M \cdot (\mu \frac{\kappa^n (1 + \alpha M)}{\kappa^n + \kappa^{n-1} + \ldots + \kappa + (1 + \alpha M)} - M) \equiv F(M) , \qquad (11)$$

where $X_i(\beta(t))$ now are the slaved variables, the evolution of which mainly depends only on the evolution of M(t). The shape of the right hand side function F(M) is depicted in Fig. 3 for several values of parameter μ.

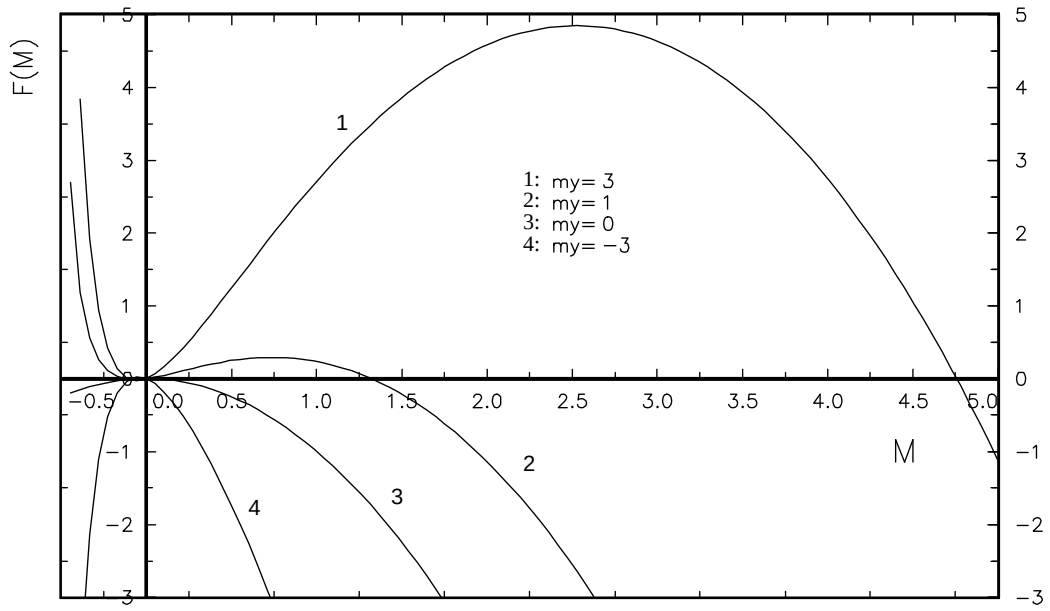

Fig. 3. Dependence of the function F(M) on M for different values of parameterμ (with n=3)

Consequently the evolution of the whole system of electron transfer reactions can for μ>0 approximately be described by one variable M, i.e. a self-organized ordering process occurs at μ=0, which imposes on the electron flux in the reaction chain a "macroscopic" ordered structure. Equation (11) we will call, by analogy to Haken's laser equation, the equation of co-operative electron transfer. This analogy can be illustrated by introducing formally a potential for the motion of the variable M:

$$\frac{dM}{dt} = - \text{grad } V(M) , \quad V(M) = \int F(M)\, dM , .$$

Then, the behaviour of M can be visualized as an overdamped motion of a ball in a one-dimensional potential with the shape V(M)[7]. The shape of the potential V(M) is shown in Fig. 4 for the same parameter values as in Fig.3.

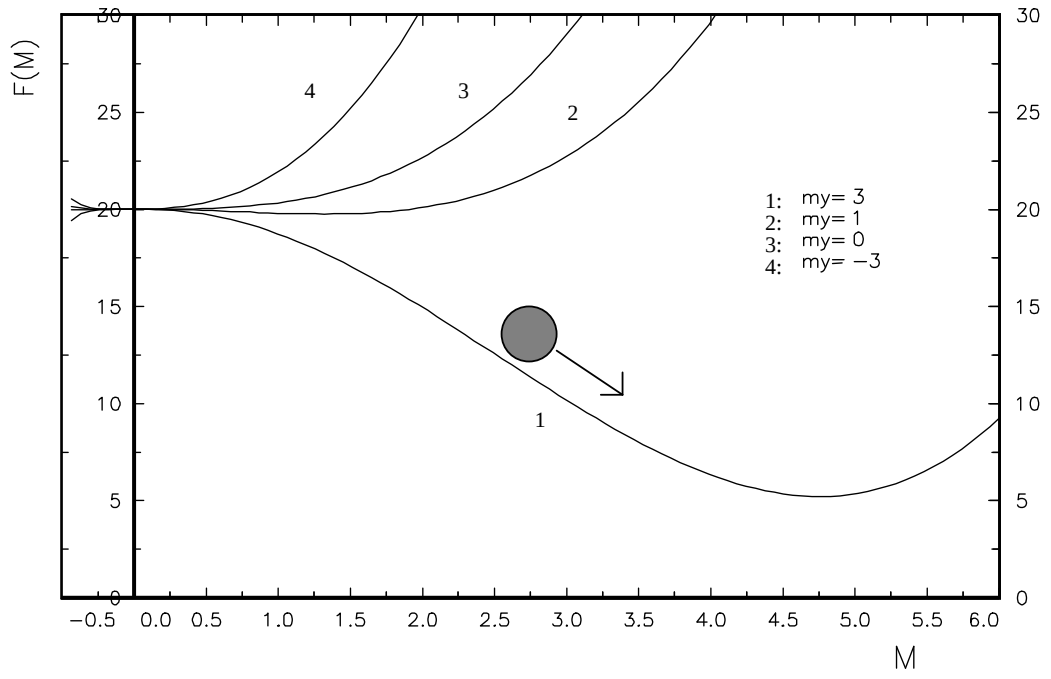

Fig. 4. Dependence of the potential function V(M) on M for different values of parameter μ (with n=3)

Here one can see that for $\mu < 0$ the potential has only one stable state (minimum) at M=0, which becomes neutral stable at $\mu = 0$ and unstable with $\mu > 0$ (maximum). Simultaneously a new minimum occurs at a value of $M > 0$, which represents the new state of co-operative electron transfer. According to equation (11) in Fig. 5 is shown the time evolution of the autocatalytic order parameter M and the corresponding value of electron flux J (which is proportional to X_n). The evolution starts in the unstable state $M = 0$ and, after a small perturbation, undergoes a rapid transition to the new stable state of cooperative and stimulated electron transfer.

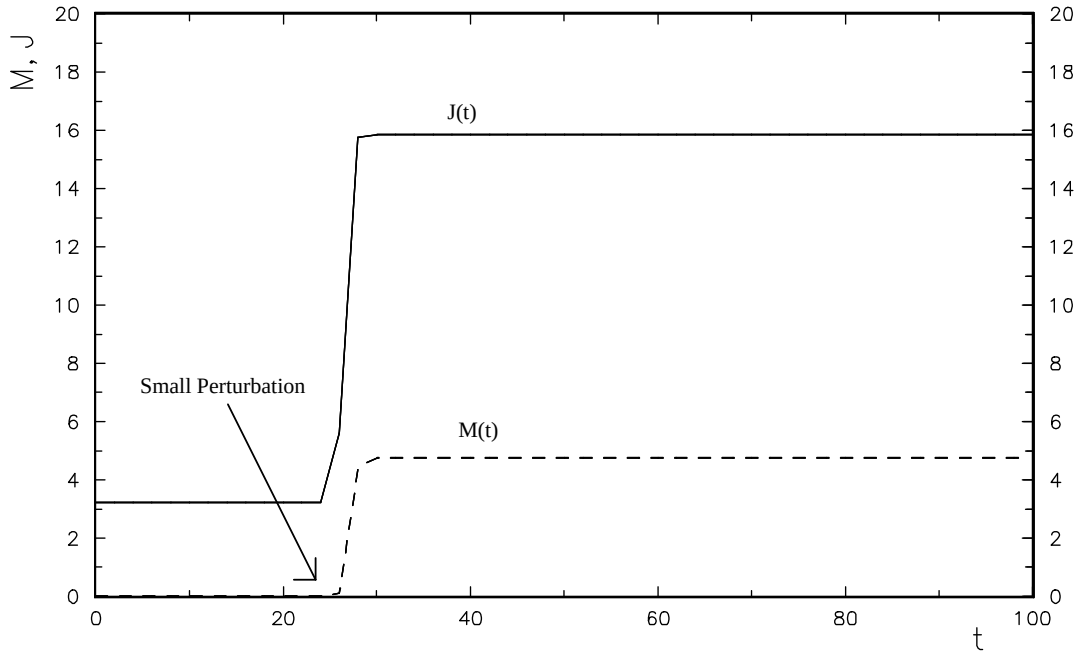

Fig. 5. Evolution of order parameter M and electron flux J (α=10, κ=1.2, μ=3 and with n=3)

It should also been noted that the autocatalytic production of the intermediate M could be of higher order than two. In the case of a third order reaction (a cubic non-linearity in M) after the bifurcation the system would have the choice between two stable states, separated by an unstable middle state. These stable states are equivalent to a highly conducting and a low conducting electron transfer pathway, respectively. Here we are dealing with a non-linear molecular electron device which could serve to build molecular computers.

5. Discussion

In the presented model we showed that stimulated and co-operative electron transfer is, in principle, possible. A molecular complex suitable for co-operative electron transfer must have suitable molecular feedback loops and autocatalytic process steps. A remarkable consequence would be the generation of a state of high electronic conductivity equivalent to a dramatic reduction of activation energies.

Such a dynamic co-operative electronic state with new electronic properties would have significant consequences for several fields including material science, energy conversion and electrocatalysis as well as for the further understanding of very effective biochemical processes.

In biology the most likely system where co-operative electron transfer is to be expected is the last step of photosynthetic oxygen evolution ($S_4 \rightarrow S_0$), which occurs very closely to the ideal thermodynamic potential of water decomposition[8] and which up to now cannot be reproduced artificially. An indication for the existence of non-linear positive feedback processes in photosynthesis is the occurrence of spontaneous oscillations in intact leaf tissue from spinach, induced by a sudden increase in ambient CO_2 concentration.[9]

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