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ORIGINAL PAPER

Quadratic first integrals of kinetic differential equations

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Abstract Classes of kinetic differential equations are delineated which do have a quadratic first integral, and classes which can not have one. Example reactions corresponding to the obtained kinetic differential equations are shown, and a few figures showing the trajectories of the corresponding systems are also included. Connections to other areas are mentioned and unsolved problems collected. The new results are theoretical, although computational tools are heavily used. Applications from biology and combustion theory will come later.

Keywords First integral · Kinetic differential equation · Computational biology and chemistry

1 Introduction

Our aim is to determine classes of mass action type kinetic differential equations with the property of having a quadratic first integral. Since the introduction of the name of first integral by E. Nöther, in 1918 it turned out that first integrals may help

- prove that the complete solution of the induced kinetic differential equation is defined for all positive times [38, p. 586, Theorem 9];

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- reduce the number of variables either by constructing an appropriate lumping scheme [17] or by simply eliminating some variables;
- apply the generalization of the Bendixson and Bendixson–Dulac criterion to higher dimensional cases [31,40].

Our main tool to find such first integrals is the comparison of coefficients of polynomials and the characterization of kinetic differential equations within the class of polynomial ones [14]. (A good review of our earlier results has been given by [3]). This characterization has proved quite useful in

- designing minimal oscillatory reactions [34],
- providing an alternative proof for the uniqueness of the Lotka–Volterra model [21,23],
- investigating chaos in chemical reactions [11,33],
- investigating symmetries in kinetic differential equations [29,32];
- selecting the kinetic lumping schemes from all the possible ones [8],
- finding necessary conditions of Turing instability [27,28].

(Let us remark in passing that Dilao [5] in his detailed analysis of Turing instability disregarded this characterization, therefore his Case f) in Theorem 2.2 cannot occur in a mass action type kinetic model).

We are also interested in kinetic differential equations with quadratic first integrals which describe mass conserving reactions [4,15,24]. It turns out in some cases that the existence of a quadratic first integral and mass conservation together form a too rigorous set of requirements: we may be able to prove that such equations do not exist.

Once we have a kinetic differential equation fulfilling some requirements we might be interested in reactions with the given induced kinetic differential equation. However, the solution to this problem is far from being unique [30, page 48–49], [6, page 67–68]. One possible approach might be that we try to find a reaction with a given property (weak reversibility, zero deficiency etc.), or a minimal or maximal reaction in a certain sense with a given property [25,26].

The structure of our paper is as follows. Section 2 presents the basic definitions. Section 3 gives the general results, both positive and negative: on the existence and nonexistence of kinetic differential equations with quadratic first integrals depending possibly on further assumptions. In some cases we also show a reaction having the obtained differential equation, and a few figures reflecting the behavior of possible trajectories. Section 4 shows how *Mathematica* (more precisely, the program package `ReactionKinetics` written in the *Mathematica* language, [20,35,36]) can be used to formulate, prove or disprove conjectures. Finally, Sect. 5 formulates problems to be solved.

2 Mass action type kinetic differential equations

Here we recapitulate very shortly the basic concepts of formal reaction kinetics as they can be found e.g. in [6,18] or [35].

2.1 Induced kinetic differential equation of a reaction with mass action type kinetics

Let us consider a vessel (a cell, a reactor, a test tube etc.) of constant volume at constant pressure and temperature and let M, $R \in \mathbb{N}$; $\alpha, \beta \in \mathbb{N}_0^{M\times R}$, and consider the **complex chemical reaction**:

$$\sum_{m=1}^{M} \alpha(m,r)X(m) \longrightarrow \sum_{m=1}^{M} \beta(m,r)X(m) \quad (r = 1, 2, \ldots, R), \tag{1}$$

where the components of the matrices $\alpha = (\alpha(m,r))_{m=1,2,\ldots,M;r=1,2,\ldots,R}$ and $\beta = (\beta(m,r))_{m=1,2,\ldots,M;r=1,2,\ldots,R}$ are the **stochiometric coefficients**. There are a few natural conditions fulfilled by the stoichiometric matrix (see e.g. [4, page 77]):

1. all the species take part in at least one reaction step;
2. all the reaction steps change the quantity of at least one species;
3. all the reaction steps are determined by their reactant and complex products.

Remark 1 The last requirement may be too restrictive because if a reaction can proceed through two different transition states, as in the reaction

$$CH_3CHOH + O_2 \leftrightharpoons HO_2 + CH_3CHO$$

[41], then one should duplicate this step to exactly represent the mechanistic details of the reaction.

Suppose the reaction can adequately be described using **mass action kinetics**, then its **deterministic model** is

$$c_m{}'(t) = f_m(\mathbf{c}(t)) := \sum_{r=1}^{R} (\beta(m,r) - \alpha(m,r))k_r \prod_{p=1}^{M} c_p(t)^{\alpha(p,r)} \tag{2}$$

$$c_m(0) = c_{m0} \in \mathbb{R}_0^+ \quad (m = 1, 2, \ldots, M) \tag{3}$$

(with the positive **reaction rate coefficients** k_r)—describing the time evolution of the concentration versus time functions

$$t \mapsto c_m(t) := [X(m)](t)$$

of the species. Equation (2) is also called the mass action type **induced kinetic differential equation** of the reaction (1).

2.2 Polynomial and kinetic differential equations

The induced kinetic differential equation of the reaction (1) is a polynomial differential equation, because all the functions f_m are polynomials in all their variables. (This

property can be shown to be equivalent with the fact that f_m is an M-variable polynomial [2]). However, it is not true that all polynomial differential equations can be obtained as induced kinetic differential equations of some reactions, as the examples

$$x' = y, \quad y' = \boxed{-x}$$

(of the harmonic oscillator), or the Lorenz model

$$x' = \sigma(y - x), \quad y' = \rho x - \boxed{xz}, \quad z' = xy - \beta z \quad (\sigma, \rho, \beta > 0)$$

show. The speciality of kinetic differential equations is that they cannot contain terms like those boxed above, i.e. terms expressing the decay of a quantity without its participation. Such terms are said to represent **negative cross effects** [14]. Moreover, it is also true that the absence of such terms allows us to construct a reaction inducing the given differential equation [14]. To formulate this property and also our statements below we need the following definition.

Definition 1 Let $M \in \mathbb{N}$, and let us suppose that $\mathbf{P} : \mathbb{R}^M \longrightarrow \mathbb{R}^M$ is a function with the property that all its coordinate functions are polynomials in all their variables. Then the differential equation

$$\mathbf{x}' = \mathbf{P} \circ \mathbf{x} \tag{4}$$

is said to be a **polynomial differential equation**.

Let us remark that $\mathbb{R}^2 \ni (x, y) \to xy$ is a second degree polynomial although it is of the first degree in all of its variables. When formulating and proving our results in Sect. 3 below we sometimes need notations different from those in the above definition for the sake of transparency.

Definition 2 Let us consider the polynomial differential equation (4), and suppose that there is an $m \in \{1, 2, \ldots, M\}$ and a vector

$$\mathbf{c}_0^m := (c_1, c_2, \ldots, c_{m-1}, 0, c_{m+1}, \ldots, c_M)$$

($c_p \geq 0$ for $p = 1, 2, \ldots, m-1, m+1, \ldots, M$) so that $P_m(\mathbf{c}_0^m) < 0$. Then, (4) is said to contain **negative cross-effect**.

Our starting point is the following statement the constructive proof of which can be found in [14].

Theorem 1 *A polynomial differential equation is the induced kinetic differential equation of a reaction endowed with mass action type kinetics if and only if it contains no negative cross-effect.*

Then, it is quite natural to call polynomial differential equations **kinetic** if they have no negative cross-effect.

Let us remark that the absence of a negative cross-effect is stronger than the property that the velocity of the vector field is always pointing into the interior of the first orthant (implying that the first orthant is an invariant set of (2)) as the remark by Feinberg (cited in [30, p. 41]) shows:

$$c_1' = c_2 + c_2^2 - 2c_2c_3 + c_3^2, \quad c_2' = 0, \quad c_3' = 0.$$

It may be useful to know that Chellaboina et al. gave practically the same example and also reproduced our proof of the above theorem in [3].

2.3 Mass conservation

Although it is very convenient to allow reactions like $X \longrightarrow 0$ to describe outflow, or those like $0 \longrightarrow X$ to represent inflow, or $X \longrightarrow 2X$ to denote autocatalysis, it is still quite natural to give extra importance to reactions which do conserve mass. The intuitive meaning of mass conservation is that calculating the total mass on both sides of a reaction step we get the same amount [15, page 89].

Definition 3 The reaction (1) is said to be **stoichiometrically mass conserving**, if there exists a vector $\varrho \in (\mathbb{R}^+)^M$ for which

$$\forall r \in \{1, 2, \ldots, R\} : \sum_{m=1}^{M} \varrho(m)\alpha(m, r) = \sum_{m=1}^{M} \varrho(m)\beta(m, r) \tag{5}$$

is fulfilled.

It is not so trivial to decide if a reaction of the form (1) is stoichiometrically mass conserving or not if we are only given the stoichiometric coefficients [4,24]. (These last papers provide sufficient and necessary conditions of, and algorithms to decide mass conservativity).

Now an equivalent definition of stoichiometric mass conservation will be given. To arrive at that definition preparations are to be made.

Definition 4 The **stochiometric subspace** of the reaction (1) is the linear space

$$\mathcal{S} := \text{span}\,\{\alpha(., r) - \beta(., r); r = 1, 2, \ldots, R\}.$$

With this, the reaction (1) is stoichiometrically mass conserving if there exists a vector with positive coordinates in the orthogonal complement of the stoichiometric subspace. The set $c_0 + \mathcal{S} \quad (c_0 \in (\mathbb{R}^+)^M)$ is a (positive) **reaction simplex**.

A fundamental result by Horn and Jackson [15] follows.

Theorem 2 *A reaction is stoichiometrically mass conserving if and only if all positive reaction simplexes are bounded.*

An immediate consequence of the theorem is that a complete solution of a stoichiometrically mass conserving system is defined for all nonnegative times. Further much more refined statements on nonnegativity can be found in [38].

Example 1 Stoichiometric mass conservation is sufficient but not necessary for the preservation of (possibly, weighted) total mass. The example [9, page 89] shows that a positive linear combination of the concentrations can be constant even if the positive coefficients do not lie in the orthogonal complement of the stoichiometric subspace. If this is the case one may speak about a **kinetically mass conserving** reaction. Let us see the details (Fig. 1).

Let all the reaction rate constants be unity. Now we are going to show that the vector $\varrho = \begin{pmatrix} 1 & 2 & 4 & 1 & 4 & 5 & 2 & 2 & 1 \end{pmatrix}^\top$ is orthogonal to the right hand side of the induced kinetic differential equation

$$\begin{aligned} a' &= -2ab + c & b' &= -2ab + c & c' &= ab - 2c \\ d' &= c - de + f & e' &= c - de + f & f' &= de - f \\ g' &= ab - g + j^2 & h' &= g - h + j^2 & j' &= 2h - 4j^2 \end{aligned}$$

of the reaction but it is not orthogonal from the left to the matrix

$$\gamma = \left(\begin{array}{c|cccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ \hline \mathrm{A} & -1 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ \mathrm{B} & -1 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ \mathrm{C} & 1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mathrm{D} & 0 & 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ \mathrm{E} & 0 & 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ \mathrm{F} & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ \mathrm{G} & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 1 \\ \mathrm{H} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 1 & 0 \\ \mathrm{J} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & -2 & -2 \end{array}\right) \tag{6}$$

of the elementary reaction vectors. Really,

$$\varrho^\top \begin{pmatrix} a' & b' & c' & d' & e' & f' & g' & h' & j' \end{pmatrix}^\top = 0,$$

and

$$\varrho^\top \gamma = \begin{pmatrix} 1 & -1 & 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \end{pmatrix}^\top \neq \mathbf{0}^\top.$$

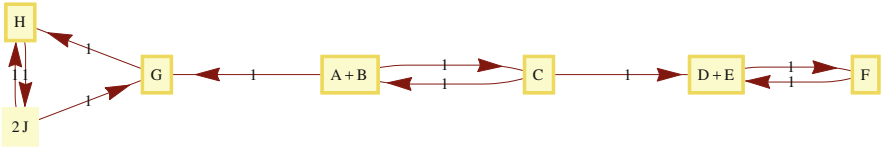


Fig. 1 The Feinberg–Horn example

It is a very natural requirement that a numerical method aimed at solving (2) should keep the total mass $\sum_{m=1}^{M} \varrho_m c_m(t)$ constant (independent on time) in case of a mass conserving reaction. There are some methods to have this property, see e.g. [1]. A similar requirement is to keep other, e.g. quadratic first integrals, what has also been shown for some methods [22].

However, not much is known about equations, especially kinetic differential equations with quadratic first integrals. Obviously, equations of mechanics, like that of the standard harmonic oscillator $x' = y \quad y' = -x$ may have quadratic first integrals, $V(p, q) := p^2 + q^2$ in this case, and here the meaning of the quadratic first integral is the total mechanical energy.

3 Existence and nonexistence of quadratic first integrals

3.1 Diagonal first integrals

Theorem 3 *Let us consider the following system of differential equations*

$$x'_m = F_m \circ (x_1, x_2, \ldots, x_M), \quad (m = 1, \ldots, M) \tag{7}$$

where the functions F_m are quadratic functions of the variables, that is,

$$F_m(x_1, x_2, \ldots, x_M) = \sum_{p=1}^{M} A_{m,p} x_p^2 + \sum_{\substack{p=1 \\ p \neq m}}^{M} B_{m,p} x_m x_p + \sum_{\substack{p,q=1 \\ p<q \\ p \neq m, q \neq m}}^{M} C_{p,q}^{m} x_p x_q + \sum_{p=1}^{M} D_{m,p} x_p + E_m. \tag{8}$$

*Suppose that the system of differential equations is **kinetic**. The function*

$$V(x_1, x_2, \ldots, x_M) = a_1 x_1^2 + a_2 x_2^2 + \cdots + a_M x_M^2$$

(with $a_m > 0$ for $m = 1, 2, \ldots, M$) is a first integral for the above system if and only if the functions F_m have the following form with $K_{m,p} \geq 0$:

$$F_m(x_1, x_2, \ldots, x_M) = \sum_{\substack{p=1 \\ p \neq m}}^{M} a_p K_{m,p} x_p^2 - \sum_{\substack{p=1 \\ p \neq m}}^{M} a_p K_{p,m} x_m x_p. \tag{9}$$

Proof The function V is a first integral for the system (7) if and only if its Lie-derivative with respect to the system is equal to zero, that is,

$$\begin{aligned} 0 &= \frac{1}{2}\sum_{m=1}^{M} \partial_m V(x_1, x_2, \ldots, x_M) F_m(x_1, x_2, \ldots, x_M) \\ &= \sum_{m=1}^{M} a_m \left(\sum_{p=1}^{M} A_{m,p} x_m x_p^2 + \sum_{\substack{p=1 \\ p\neq m}}^{M} B_{m,p} x_m^2 x_p \right. \\ &\quad \left. + \sum_{\substack{m\neq p, m\neq q \\ p<q}} C_{p,q}^{m} x_m x_p x_q + \sum_{p=1}^{M} D_{m,p} x_m x_p + E_m x_m \right) \end{aligned} \tag{10}$$

Since the system (7) is kinetic, the coefficients of terms in F_m not containing x_m are nonnegative:

$$\begin{aligned} &(k1)\ A_{m,p} \geq 0 \text{ for } m, p \quad = 1, 2, \ldots M;\ m \neq p \\ &(k2)\ C_{p,q}^{m} \geq 0 \text{ for } m, p, q = 1, 2, \ldots M;\ m \neq p, m \neq q, p < q \\ &(k3)\ D_{m,p} \geq 0 \text{ for } m, p \quad = 1, 2, \ldots M;\ m \neq p \\ &(k4)\ E_m \quad \geq 0 \text{ for } m \qquad = 1, 2, \ldots M. \end{aligned}$$

For all m, the coefficients of x_m^3, x_m^2 and x_m are $a_m A_{m,m}$, $a_m D_{m,m}$ and $a_m E_{m,m}$, respectively. Since these monomials are independent of each other and of the other terms in (10), it follows that $A_{m,m} = D_{m,m} = E_{m,m} = 0$.

If $m \neq p$, then the monomial $x_m x_p$ appears twice in (10) with coefficients $a_m D_{m,p}$ and $a_p D_{p,m}$. Thus $a_m D_{m,p} + a_p D_{p,m} = 0$ and because of $(k3)$, $D_{m,p} = D_{p,m} = 0$.

If $m \neq p, m \neq q, p < q$, then the monomial $x_m x_p x_q$ appears three times in (10) with coefficients $a_m C_{p,q}^{m}$, $a_p C_{m,q}^{p}$ and $a_q C_{m,p}^{q}$. Thus $a_m C_{p,q}^{m} + a_p C_{m,q}^{p} + a_q C_{m,p}^{q} = 0$ and because of $(k2)$, $C_{p,q}^{m} = C_{m,q}^{p} = C_{m,p}^{q} = 0$.

If $m \neq p$, then the monomial $x_m x_p^2$ appears twice in (10) with coefficients $a_m A_{m,p}$ and $a_p B_{p,m}$ and thus $a_m A_{m,p} + a_p B_{p,m} = 0$ where $A_{m,p} \geq 0$ because of $(k1)$. Without the loss of generality, it may be assumed that $A_{m,p} = a_p K_{m,p}$ where $K_{m,p} \geq 0$ and so $B_{p,m} = -a_m K_{m,p}$.

The the proof of the **if** part is obvious. □

Example 2 Let $M = 2$ and suppose that $V(x, y) = x^2 + y^2$. Then (9) specializes to

$$x' = ay^2 - bxy, \quad y' = bx^2 - axy \tag{11}$$

which may be considered as the induced kinetic differential equation of the reaction

$$\mathrm{X} \xleftarrow{a} \mathrm{X} + \mathrm{Y} \xrightarrow{b} \mathrm{Y} \qquad 2\mathrm{X} \xrightarrow{b} 2\mathrm{X} + \mathrm{Y} \qquad 2\mathrm{Y} \xrightarrow{a} \mathrm{X} + 2\mathrm{Y} \tag{12}$$

as the application of `RightHandSide[{X <-X + Y -> Y, 2 X -> 2 X + Y, 2 Y -> X + 2 Y},{a, b, b, a}, {x, y}]` gives: $\{ay^2 - bxy, bx^2 - axy\}$. A typical trajectory is shown in Fig. 3a. Naturally arises the question if the differential equation (11) can be represented with a mechanism only containing three complexes 2X, 2Y, X + Y. It can be easily shown that the answer is negative.

Example 3 Let $M = 3$ and suppose that $V(x, y, z) = x^2 + y^2 + z^2$. Then (9) specializes to

$$\begin{aligned} x' &= ay^2 + bz^2 - cxy - exz \\ y' &= cx^2 + dz^2 - axy - fyz \\ z' &= ex^2 + fy^2 - bxz - dyz \end{aligned} \tag{13}$$

(with nonnegative coefficients a, b, c, d, e, f) which may be considered as the induced kinetic differential equation of the reaction shown in Fig. 2. as again the application of `RightHandSide` verifies. A typical trajectory is shown in Fig. 3b.

Corollary 1 *As the divergence of the system* (13) *is* $-ax - bx - cy - dy - ez - fz < 0$ *in the first orthant and the system has a first integral, [31, Theorem 3.3] (actually, a version of K. R. Schneider's theorem) implies that it has no periodic orbit in the first orthant.*

The next result shows that (even weighted) sum of squares cannot be a first integral if mass is conserved.

Theorem 4 *Let us consider the differential equation system* (7) *where the functions* F_m *are of the form* (8). *Suppose that the differential equation system is* ***kinetic*** *and* ***kinetically mass conserving***. *The function*

$$V(x_1, x_2, \ldots, x_M) = a_1 x_1^2 + a_2 x_2^2 + \cdots + a_M x_M^2$$

(where $a_m \neq 0$ *for all* m*) is a first integral for the system* (7), *if and only if for all* m*:*

$$F_m(x_1, x_2, \ldots, x_M) = 0.$$

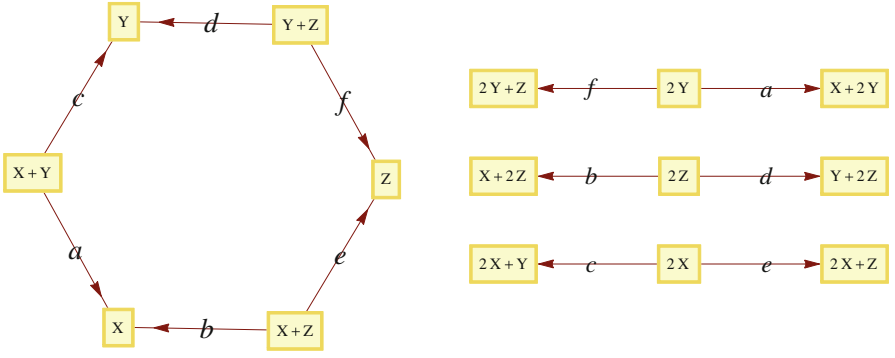


Fig. 2 3D system with a quadratic first integral

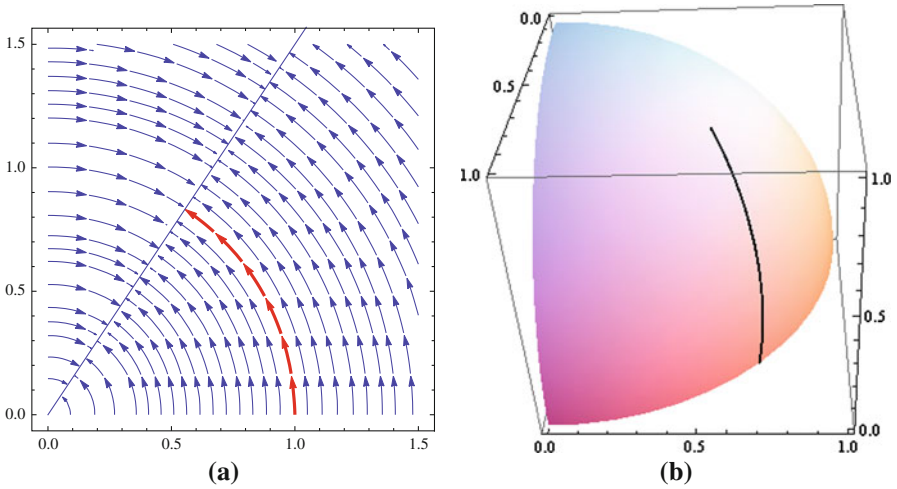


Fig. 3 **a** Trajectories of system (11) with $a = 2, b = 3$ starting from $x(0) = 1, y(0) = 0$. **b** Trajectories of system (13) with $a = 2, b = 3, c = 4, d = 5, e = 6, f = 7$ starting from $x(0) = \frac{1}{\sqrt{2}}, y(0) = \frac{1}{\sqrt{2}}, z(0) = 0$

Proof The function V is a first integral for the system (7) if and only if (10) holds. Since the system (7) is kinetic and mass conserving with some positive numbers $\varrho_m, m = 1, 2, \ldots, M$; besides $(k1) - (k4)$ the following inequalities also hold:

$$
\begin{aligned}
&(m1) \text{ for all } m \quad \textstyle\sum_{p=1}^{M} \varrho_p A_{p,m} = 0 \text{ (the sum of the coefficients of } x_m^2) \\
&(m2) \text{ for all } m, p \ \varrho_m B_{m,p} + \varrho_p B_{p,m} + \sum_{\substack{q=1 \\ q\neq m, q\neq p}}^{M} \varrho_q C_{m,p}^{q} = 0 \\
&\qquad \text{(the sum of the coefficients of } x_m x_p) \\
&(m3) \text{ for all } m \quad \textstyle\sum_{p=1}^{M} \varrho_p D_{p,m} = 0 \text{ (the sum of the coefficients of } x_m) \\
&(m4) \text{ for all } m \quad \textstyle\sum_{m=1}^{M} \varrho_m E_m = 0.
\end{aligned}
$$

Similarly, as in the proof of Theorem 3, for all $m : A_{m,m} = 0,\ D_{m,m} = 0$ and $E_m = 0$. Then, for all $m \neq p$, because of $(k1)$ and $(m1) : A_{m,p} = 0$, and because of $(k3)$ and $(m3) : D_{m,p} = 0$.

If $m \neq p$, then the coefficient of $x_m^2 x_p$ in (10) is $a_m B_{m,p} + a_p A_{p,m} = 0$. Since $A_{p,m} = 0$, it follows that for all $m, p, m \neq p : B_{p,m} = 0$. Finally, because of $(k2)$ and $(m2)$, for all m, p, q such that $q \neq m, q \neq p, m < p : C_{m,p}^{q} = 0$.

The proof of the **if** part is obvious. □

Theorem 5 *Let us consider the following differential equation system*

$$
\begin{aligned}
x_k' &= X_k \circ (x_1, \ldots, x_K, y_1, \ldots, y_L, z), \quad (k = 1, \ldots, K) \\
y_l' &= Y_l \circ (x_1, \ldots, x_K, y_1, \ldots, y_L, z), \quad (l = 1, \ldots, L) \\
z' &= Z \circ (x_1, \ldots, x_K, y_1, \ldots, y_L, z)
\end{aligned} \tag{14}
$$

where the functions X_k, Y_l, Z are quadratic polynomials of all the variables and K, L are positive integers. Suppose that the differential equation system is ***kinetic*** *and* ***kinetically mass conserving*** *with some positive numbers $\varrho_k^x, \varrho_l^y, \varrho^z$. ($k = 1, \ldots, K, l = 1, \ldots, L$). The function*

$$V(x_1, \ldots, x_K, y_1, \ldots, y_L, z) = a_1 x_1^2 + \ldots a_K x_K^2 - b_1 y_1^2 - \ldots b_L y_L^2$$

(where $a_k > 0$ and $b_l > 0$ for all k, l) is a first integral for system (14) if and only if

$$X_k(x_1, \ldots, x_K, y_1, \ldots, y_L, z) = \sum_{l=1}^{L} b_l A_{k,l} y_l z, \quad (k = 1, \ldots, K)$$

$$Y_l(x_1, \ldots, x_K, y_1, \ldots, y_L, z) = \sum_{k=1}^{K} a_k A_{k,l} x_k z, \quad (l = 1, \ldots, L)$$

$$Z = -\left(\sum_{k=1}^{K} \varrho_k^x X_k + \sum_{l=1}^{L} \varrho_l^y Y_l \right)$$

where $A_{k,l} \geq 0$ for all k, l. If $K = 0$ or $L = 0$, then $X_k = Y_l = Z = 0$.

Proof The function V is a first integral for the system (14) if and only if the Lie-derivative is equal to zero, that is,

$$\sum_{k=1}^{K} a_k x_k X_k(x_1, \ldots, x_K, y_1, \ldots, y_L, z) - \sum_{l=1}^{L} b_l y_l Y_l(x_1, \ldots, x_K, y_1, \ldots, y_L, z) = 0 \tag{15}$$

It is obvious that the functions X_k, Y_l, Z may not contain constant terms. Since the system (14) is kinetic and mass conserving, the constants are nonnegative and their weighted sum with positive weights is equal to zero, and thus each constant is equal to zero.

Next we show that the terms x_k^2, y_l^2, z^2 and x_k, y_l, z in X_k, Y_l, Z have zero coefficients for all k, l. Let us consider at first only the terms containing quadratic and linear monomials.

$$X_k = \left(\sum_{i=1}^{K} A_{k,i}^x x_i^2 + \sum_{j=1}^{L} B_{k,j}^x y_j^2 + C_k^x z^2 \right) + \left(\sum_{i=1}^{K} \overline{A}_{k,i}^x x_i + \sum_{j=1}^{L} \overline{B}_{k,j}^x y_j + \overline{C}_k^x z \right) + \ldots$$

$$Y_l = \left(\sum_{m=1}^{K} A_{l,m}^y x_m^2 + \sum_{n=1}^{L} B_{l,n}^y y_n^2 + C_l^y z^2 \right) + \left(\sum_{m=1}^{K} \overline{A}_{l,m}^y x_m + \sum_{n=1}^{L} \overline{B}_{l,n}^y y_n + \overline{C}_l^y z \right) + \ldots$$

$$Z = \left(\sum_{k=1}^{K} A_k^z x_k^2 + \sum_{l=1}^{L} B_l^z y_l^2 + C^z z^2 \right) + \left(\sum_{k=1}^{K} \overline{A}_k^z x_k + \sum_{l=1}^{L} \overline{B}_l^z y_l + \overline{C}^z z \right) + \ldots \tag{16}$$

□

(a) The coefficients of x_k^3 and y_l^3 in (15) are $a_k A_{k,k}^x$ and $-b_l B_{l,l}^y$, respectively, and so for all k, l : $A_{k,k}^x = B_{l,l}^y = 0$. Because of mass conservation, the weighted sums of the coefficients of x_k^2 and y_l^2 in (16) are equal to zero, that is,

$$\sum_{s=1,s\neq k}^{K} \varrho_s^x A_{s,k}^x + \sum_{t=1}^{L} \varrho_t^y A_{t,l}^y + \varrho^z A_k^z = 0 \quad \text{for all } 1 \le k \le K$$

$$\sum_{s=1}^{K} \varrho_s^x B_{s,k}^x + \sum_{t=1,t\neq l}^{L} \varrho_t^y B_{t,l}^y + \varrho^z B_l^z = 0 \quad \text{for all } 1 \le l \le L$$

Since the system (14) is kinetic, each term in the above sums is nonnegative, therefore each coefficient of x_k^2 and y_l^2 in (16) is equal to zero. The coefficients of $x_k z^2$ and $y_l z^2$ in (15) are $a_k C_k^x$ and $-b_l C_l^y$, respectively, and so for all k, l : $C_k^x = C_l^y = 0$. Therefore, because of mass conservation, $C^z = 0$ as well.

(b) The coefficients of x_k^2 and y_l^2 in (15) are $a_k \overline{A}_{k,k}^x$ and $-b_l \overline{B}_{l,l}^y$, respectively, therefore $\overline{A}_{k,k}^x = \overline{B}_{l,l}^y = 0$. It can be shown very similarly as in part (a) that the coefficients of x_k, y_l, z in X_k, Y_l, Z are equal to zero as well.

(c) Next consider the terms of the form $x_s x_t$, $y_s y_t$ and $x_i y_j$ (where $s < t$) in X_k, Y_l, Z. We show that these terms have zero coefficients as well for all s, t, i, j, where $s < t$.

$$\begin{aligned}
X_k &= \sum_{\substack{s,t=1\\ s<t}}^{K} D_{s,t}^{x,k} x_s x_t + \sum_{\substack{s,t=1\\ s<t}}^{L} E_{s,t}^{x,k} y_s y_t + \sum_{\substack{1\le s\le K\\ 1\le t\le L}} F_{s,t}^{x,k} x_s y_t + \dots \\
Y_l &= \sum_{\substack{s,t=1\\ s<t}}^{K} D_{s,t}^{y,l} x_s x_t + \sum_{\substack{s,t=1\\ s<t}}^{L} E_{s,t}^{y,l} y_s y_t + \sum_{\substack{1\le s\le K\\ 1\le t\le L}} F_{s,t}^{y,l} x_s y_t + \dots \\
Z &= \sum_{\substack{s,t=1\\ s<t}}^{K} D_{s,t}^{z} x_s x_t + \sum_{\substack{s,t=1\\ s<t}}^{L} E_{s,t}^{z} y_s y_t + \sum_{\substack{1\le s\le K\\ 1\le t\le L}} F_{s,t}^{z} x_s y_t + \dots
\end{aligned} \tag{17}$$

For all $s < t$ the coefficients of $x_s^2 x_t$, $x_s x_t^2$, $y_s^2 y_t$ and $y_s y_t^2$ in (15) are $a_s D_{s,t}^{x,s}$, $a_t D_{s,t}^{x,t}$, $-b_s E_{s,t}^{y,s}$ and $-b_t E_{s,t}^{y,t}$, respectively, and so $D_{s,t}^{x,s} = D_{s,t}^{x,t} = E_{s,t}^{y,s} = E_{s,t}^{y,t} = 0$. Since the system is kinetic and because of mass conservation, for all $1 \le k < l \le K$, $\sum_{\substack{i=1\\ i\neq k,l}}^{K} \varrho_i^x D_{k,l}^{x,i} + \sum_{j=1}^{L} \varrho_j^y D_{k,l}^{y,j} + \varrho^z D_{k,l}^z = 0$ and for all $1 \le m < n \le L$, $\sum_{i=1}^{K} \varrho_i^x E_{m,n}^{x,i} + \sum_{\substack{j=1\\ j\neq m,n}}^{L} \varrho_j^y E_{m,n}^{y,j} + \varrho^z E_{m,n}^z = 0$ where each term in the sums is nonnegative and thus the coefficients of the terms $x_s x_t$ and $y_s y_t$ ($s < t$) are equal to zero.

(d) The coefficients of $x_k^2 y_l$ and $x_k y_l^2$ ($1 \le k \le K$, $1 \le l \le L$) in (15) are $a_k F_{k,l}^{x,k}$ and $-b_l F_{k,l}^{y,l}$, respectively, and so for all k, l: $F_{k,l}^{x,k} = F_{k,l}^{y,l} = 0$. Since the system is kinetic, and because of mass conservation, $\sum_{\substack{i=1 \\ i \neq k}}^{K} \varrho_i^x F_{k,l}^{x,i} + \sum_{\substack{j=1 \\ j \neq l}}^{L} \varrho_j^y F_{k,l}^{y,j} + \varrho^z F_{k,l}^z = 0$ where each term in the sum is nonnegative. Therefore, each coefficient of $x_k y_l$ in (17) is equal to zero.

Now we may suppose that X_k, Y_l, Z have the following form:

$$\begin{aligned} X_k &= \sum_{s=1}^{K} G_{k,s}^x x_s z + \sum_{s=1}^{L} H_{k,s}^x y_s z \\ Y_l &= \sum_{s=1}^{K} G_{l,s}^y x_s z + \sum_{s=1}^{L} H_{l,s}^y y_s z \\ Z &= \sum_{s=1}^{K} G_s^z x_s z + \sum_{s=1}^{L} H_s^z y_s z \end{aligned} \tag{18}$$

(e) The coefficients of $x_k^2 z$ and $y_l^2 z$ in (15) are $a_k G_{k,k}^x$ and $-b_l H_{l,l}^y$, respectively, thus $G_{k,k}^x = 0$ and $H_{l,l}^y = 0$ for all k, l ($1 \le k \le K$, $1 \le l \le L$). The coefficient of $x_k x_l z$ ($k \neq l$) in (15) is $a_k G_{k,l}^x + a_l G_{l,k}^x = 0$. Since the system is kinetic, $G_{k,l}^x$ and $G_{l,k}^x$ are nonnegative and thus these coefficients are equal to zero for all k, l ($1 \le k \le K$, $1 \le l \le K$, $k \neq l$). Similarly, $H_{j,s}^y = 0$ for all $1 \le j \le L$, $1 \le s \le L$, $j \neq s$.

(f) Finally, the coefficients of $x_k y_l z$ in (15) is $a_k H_{k,l}^x - b_l G_{l,k}^y = 0$ where $H_{k,l}^x$ and $G_{l,k}^y$ are nonnegative for all k, l ($1 \le k \le K$, $1 \le l \le L$). Whithout the loss of generality, it may be assumed that $H_{k,l}^x = b_l A_{k,l}$ where $A_{k,l} \ge 0$. Thus $G_{l,k}^y = a_k A_{k,l}$. Using that the system is kinetically mass conserving, we obtain the formula for Z.

(g) If $K = 0$ or $L = 0$, then it can be shown easily that $X_k = Y_l = Z = 0$. If for example $L = 0$, then the same proof can be repeated with $b_l = -c_l$ where $c_l > 0$. Then in case (f) $a_k H_{k,l}^x + c_l G_{l,k}^y = 0$ where $a_k > 0$, $c_l > 0$, $H_{k,l}^x \ge 0$, $G_{l,k}^y \ge 0$ and thus $H_{k,l}^x = G_{l,k}^y = 0$.

Example 4 If $V(x, y, z) = x^2 - y^2$ and $\varrho^x = \varrho^y = \varrho^z = 1$, then the equation system is ($a \ge 0$):

$$\begin{aligned} x' &= ayz \\ y' &= axz \\ z' &= -axz - ayz \end{aligned} \tag{19}$$

A possible reaction is the following:

$$\mathrm{X} + \mathrm{Z} \xrightarrow{a} \mathrm{X} + \mathrm{Y} \xleftarrow{a} \mathrm{Y} + \mathrm{Z}$$

Example 5 If $V(x_1, x_2, y_1, y_2, z) = x_1^2 + x_2^2 - y_1^2 - y_2^2$ and $\varrho_1^x = \varrho_2^x = \varrho_1^y = \varrho_2^y = \varrho^z = 1$, then the equation system is ($a, b, c, d \geq 0$):

$$\begin{aligned} x_1' &= ay_1z + by_2z \qquad y_1' = ax_1z + cx_2z \\ x_2' &= cy_1z + dy_2z \qquad y_2' = bx_1z + dx_2z \\ z' &= -x_1' - x_2' - y_1' - y_2' \end{aligned} \tag{20}$$

A possible reaction is the following:

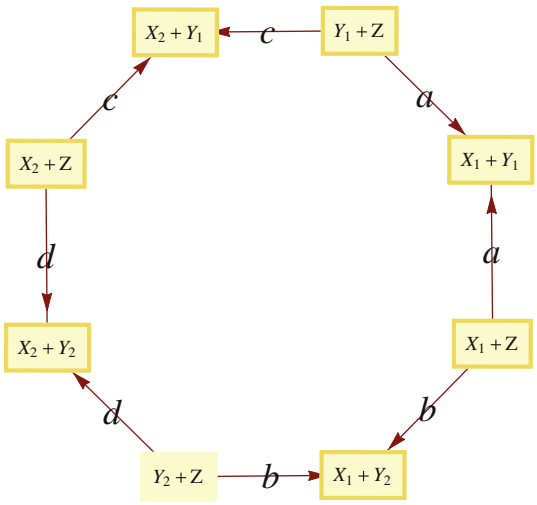
$$\begin{aligned} \mathrm{X_1 + Z} &\xrightarrow{1} \mathrm{aY_1 + bY_2 + X_1 + (1 - a - b)Z} \\ \mathrm{X_2 + Z} &\xrightarrow{1} \mathrm{cY_1 + dY_2 + X_2 + (1 - c - d)Z} \\ \mathrm{Y_1 + Z} &\xrightarrow{1} \mathrm{aX_1 + cX_2 + Y_1 + (1 - a - c)Z} \\ \mathrm{Y_2 + Z} &\xrightarrow{1} \mathrm{bX_1 + dX_2 + Y_2 + (1 - b - d)Z} \end{aligned}$$

Another possible reaction can be seen in Fig. 4.

3.2 The first integral is a binary quadratic form

Now we investigate first integrals that are quadratic homogeneous polynomials in two variables, that is, $V(x, y) = ax^2 + 2bxy + cy^2$. Obviously, if V is a first integral for a system, then any nonnegative constant multiples of it is also a first integral for the same system. Thus, without the loss of generality, it may be assumed that $a > 0$ and $b \neq 0$. Consider the following differential equation system

Fig. 4 Reaction system for (20)



$$x' = A_1x^2 + B_1xy + C_1y^2 + D_1x + E_1y + F_1$$
$$y' = A_2x^2 + B_2xy + C_2y^2 + D_2x + E_2y + F_2 \tag{21}$$

and suppose that the differential equation system is **kinetic**. Then the following statements hold.

Theorem 6 *The function $V(x, y) = ax^2 + 2bxy + cy^2$ where $a > 0$, $c > 0$, $ac - b^2 \neq 0$ is a first integral for the system (21), if and only if it has the following form ($K \geq 0, L \geq 0$):*

$$x' = -bKx^2 + (-cK + bL)xy + cLy^2$$
$$y' = aKx^2 + (bK - aL)xy - bLy^2 \tag{22}$$

If the system (22) is kinetically mass conserving then $x' = y' = 0$.

Theorem 7 *The function $V(x, y) = ax^2 + 2bxy + cy^2$ where $a > 0$, $b > 0$, $c > 0$, $ac - b^2 = 0$ is a first integral for the system (21), if and only if it has the following form ($K \geq 0, L \geq 0, M \geq 0, N \geq 0$, S is arbitrary):*

$$x' = -bKx^2 + cSxy + cLy^2 - bMx + cNy$$
$$y' = aKx^2 - bSxy - bLy^2 + aMx - bNy \tag{23}$$

If the system (23) is kinetically mass conserving with some positive numbers ϱ_1, ϱ_2 then it has the form

$$x' = -\varrho_2Kx^2 + \varrho_2Sxy + \varrho_2Ly^2 - \varrho_2Mx + \varrho_2Ny$$
$$y' = \varrho_1Kx^2 - \varrho_1Sxy - \varrho_1Ly^2 + \varrho_1Mx - \varrho_1Ny \tag{24}$$

Theorem 8 *The function $V(x, y) = ax^2 - 2bxy + cy^2$ where $a > 0$, $b > 0$, $c > 0$, $ac - b^2 = 0$ is a first integral for the system (21), if and only if it has the following form ($K \geq 0, L \geq 0, M \geq 0, N \geq 0, R \geq 0$, S is arbitrary):*

$$x' = bKx^2 + cSxy + cLy^2 + bMx + cNy + cR$$
$$y' = aKx^2 + bSxy + bLy^2 + aMx + bNy + bR \tag{25}$$

If the system (25) is kinetically mass conserving then $x' = y' = 0$.

Theorem 9 *The function $V(x, y) = ax^2 + 2bxy - cy^2$ where $a > 0$, $c > 0$, $b \neq 0$ is a first integral for the system (21), if and only if it has the following form ($K \geq 0, L \geq 0, M \geq 0$):*

$$x' = -bKx^2 + (cK - bL)xy + cLy^2 - bMx + cMy$$
$$y' = aKx^2 + (bK + aL)xy + bLy^2 + aMx + bMy \tag{26}$$

If the system (26) is kinetically mass conserving then $x' = y' = 0$.

Theorem 10 *The function $V(x, y) = ax^2 + 2bxy$ where $a > 0$, $b \neq 0$ is a first integral for the system (21), if and only if it has the following form ($K \geq 0$, $M \geq 0$, S is arbitrary):*

$$\begin{aligned} x' &= -bKx^2 - \quad bSxy \quad - bMx \\ y' &= aKx^2 + (bK + aS)xy + bSy^2 + aMx + bMy \end{aligned} \tag{27}$$

If the system (27) is kinetically mass conserving then $x' = y' = 0$.

Proof of Theorem 6 The function V is a first integral for the system (21) if and only if its Lie-derivative with respect to the system is equal to zero, that is,

$$\frac{1}{2}\left((2ax + 2by)x' + (2bx + 2cy)y'\right) = 0 \tag{28}$$

Equations $(i) - (ix)$ hold since the coefficients of the following monomials in (28) are equal to zero and (x) holds since the system kinetic:

$$\begin{array}{lll} (i) & x^3: & aA_1 + bA_2 = 0 \\ (ii) & y^3: & bC_1 + cC_2 = 0 \\ (iii) & x^2y: & bA_1 + aB_1 + cA_2 + bB_2 = 0 \\ (iv) & xy^2: & bB_1 + aC_1 + cB_2 + bC_2 = 0 \\ (v) & x^2: & aD_1 + bD_2 = 0 \\ (vi) & y^2: & bE_1 + cE_2 = 0 \\ (vii) & xy: & bD_1 + aE_1 + cD_2 + bE_2 = 0 \\ (viii) & x: & aF_1 + bF_2 = 0 \\ (ix) & y: & bF_1 + cF_2 = 0 \\ (x) & & C_1 \geq 0, E_1 \geq 0, F_1 \geq 0, A_2 \geq 0, D_2 \geq 0, F_2 \geq 0 \end{array}$$

Since $A_2, C_1 \geq 0$, without the loss of generality, it can be assumed that $A_2 = aK$ and $C_1 = cL$ where $K, L \geq 0$. Thus, because of (i) and (ii), $A_1 = -bK$ and $C_2 = -bL$. Substituting these into (iii) and (iv) gives

$$aB_1 + bB_2 = -(ac - b^2)K, \quad bB_1 + cB_2 = -(ac - b^2)L$$

Since $ac - b^2 \neq 0$, the unique solution of this equation system is $B_1 = -cK + bL$ and $B_2 = bK - aL$.

In (v) and (vi), let $D_2 := aM$ and $E_1 := cN$ where $M, N \geq 0$. Thus, $D_1 = -bM$ and $E_2 = -bN$. Substituting these into (vii) gives $(ac - b^2)(M + N) = 0$. Since $ac - b^2 \neq 0$, it follows that $M = N = 0$ and thus $D_1 = D_2 = E_1 = E_2 = 0$. Finally, the unique solution of the system $(viii) - (ix)$ is $F_1 = F_2 = 0$.

If, moreover, the system (22) is kinetically mass conserving, then there exist positive numbers ϱ_1 and ϱ_2 such that the following equalities hold:

$$\begin{aligned} &(xi) \quad K(-\varrho_1 b + \varrho_2 a) = 0 \\ &(xii) \quad K(-\varrho_1 b + \varrho_2 a) + L(\varrho_1 b - \varrho_2 a) = 0 \\ &(xiii) \quad L(\varrho_1 c - \varrho_2 b) = 0 \end{aligned}$$

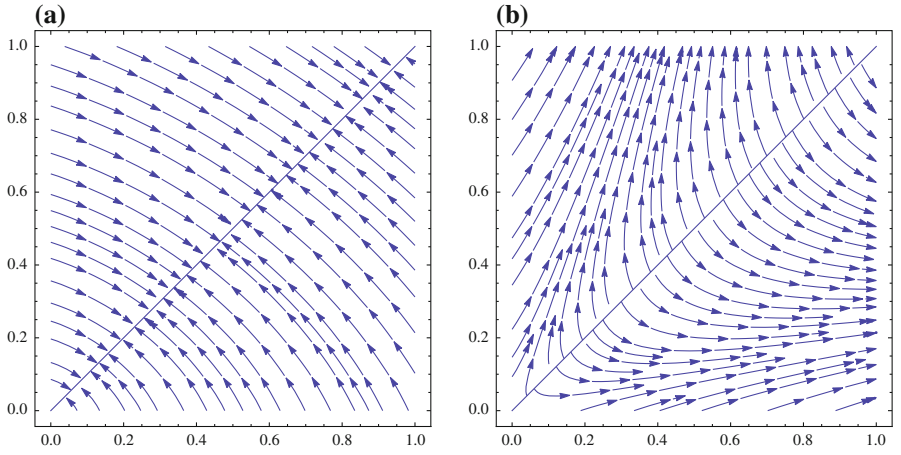


Fig. 5 Trajectories for Examples 6 and 7 **a** $a = 2, b = 1, c = 3, K = 1, L = 1$, **b** $a = 1, b = -3, c = 2, K = 1, L = 1$

If $K \neq 0$ and $L \neq 0$ then from (xi) and $(xiii)$ it follows that $ac - b^2 = 0$ which is a contradiction. If, for example, $K \neq 0$ and $L = 0$ then from (xi) and (xii) we obtain the same. Thus, $K = L = 0$.

Theorems 7–10 can be proved very similarly. □

Remark 2 The stationary points of system (22) are (1) $(x, y) = (0, 0)$; (2) if $L \neq 0$ and $K \neq 0$, then $y = \frac{K}{L}x$; (3) if $L = 0$, then $x = 0$; (4) if $K = 0$, then $y = 0$. If $ac - b^2 > 0$, then the trajectories lie on an ellipse while if $ac - b^2 < 0$, then the trajectories lie on a hyperbola as shown in Fig. 5a, b. Examples for reactions and trajectories for system (22) are:

Example 6 If $a = 2, b = 1, c = 3, K = 1, L = 1$ then the system is

$$x' = -x^2 - 2xy + 3y^2$$
$$y' = 2x^2 - xy - y^2$$

A possible reaction is the following:

$$2\mathrm{X} + \mathrm{Y} \overset{2}{\leftarrow} 2\mathrm{X} \overset{1}{\rightarrow} \mathrm{X} \overset{1}{\leftarrow} \mathrm{X} + \mathrm{Y} \overset{2}{\rightarrow} \mathrm{Y} \overset{1}{\leftarrow} 2\mathrm{Y} \overset{3}{\rightarrow} \mathrm{X} + 2\mathrm{Y}$$

Example 7 If $a = 2, b = -3, c = 2, K = 1, L = 1$ then the system is

$$x' = 3x^2 - 5xy + 2y^2$$
$$y' = x^2 - 4xy + 3y^2$$

A possible reaction is the following:

$$\begin{aligned} &2\mathrm{X} + \mathrm{Y} \overset{1}{\leftarrow} 2\mathrm{X} \overset{3}{\rightarrow} 3\mathrm{X} \\ &\mathrm{X} + 2\mathrm{Y} \overset{2}{\leftarrow} 2\mathrm{Y} \overset{3}{\rightarrow} \mathrm{Y} \\ &\mathrm{X} \overset{4}{\leftarrow} \mathrm{X} + \mathrm{Y} \overset{5}{\rightarrow} \mathrm{Y} \end{aligned}$$

3.3 Shifted sum of squares

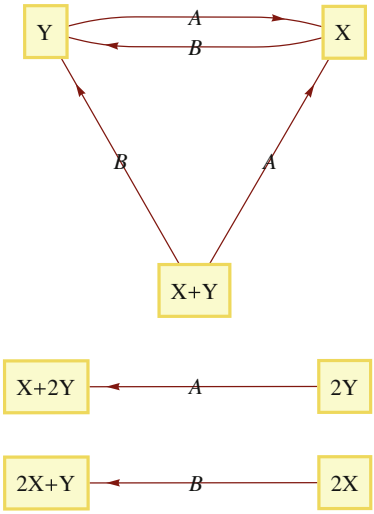
Theorem 11 *Let us consider the differential equation system (21). Suppose that this system is* ***kinetic****. The function* $V(x, y) = (x + a)^2 + (x + b)^2$ *is a first integral for the system (21) if and only if it has the following form:*

$$\begin{aligned} x' &= Ay(y + b) - Bx(y + b) = Ay^2 - Bxy - bBx + bAy \\ y' &= Bx(x + a) - Ay(x + a) = Bx^2 - Axy + aBx - aAy \end{aligned} \tag{29}$$

where $A \geq 0, B \geq 0, a \geq 0, b \geq 0$. *If* $a < 0$, *then* $B = 0$, *and if* $b < 0$, *then* $A = 0$. *From this it follows that there are no periodic orbits in the first orthant.*

If $V(x, y) = (x + 1)^2 + (y + 1)^2$, then the equations and the reactions are

$$\begin{aligned} x' &= Ay^2 - Bxy - Bx + Ay \\ y' &= Bx^2 - Axy + Bx - Ay \end{aligned}$$



4 Computer help

Finally let us mention that most of our statements can be obtained using either the *Mathematica* package `ReactionKinetics` [20,35] or by simple additional programs. E.g. the following simple code checks if negative cross effect is present in a polynomial or not.

```
   CrossEffectQ[polyval_, vars_]:= Module[{M=Length[vars]},
And @@ (Map[Not[Negative[#]] &, Flatten[MapThread[ReplaceAll,
       {MonomialList[polyval, vars],Thread[vars->#] & /@
                (1 - IdentityMatrix[M])}]]])].
```

And now let us use the newly defined function.

```
CrossEffectQ[{d, c-4yx^2+5xy+6z+7w, ax+2y, -bxy},{x,y,z,w}]
```

The answer is as expected depending on the signs of the parameters.

```
!Negative[d]   &&   !Negative[c] && !Negative[a] && !Negative[-b]
```

A more easily readable version leads to the same result.

```
CrossEffectQ2[polyval_, vars_] :=Module[{M = Length[vars], L},
           L[i_] := If[Head[polyval[[i]]] === Plus,
 Apply[List, polyval[[i]]], {polyval[[i]]}] /. MapThread[Rule,
     {vars, ReplacePart[ConstantArray[1, M], {i} -> 0]}];
    And @@ Map[# >= 0 &, Flatten[Table[L[i], {i, 1, M}]]]]
```

Using this function for the same example

```
CrossEffectQ2[{d, c-4yx^2+5xy+6z+7w, ax+2y, -bxy},{x,y,z,w}]
```

we obtain the following result

```
d >= 0  &&  c >= 0 && a >= 0 && -b >= 0
```

5 Discussion and outlook

5.1 Other types of first integrals

We wonder if it is possible to fully characterize those kinetic differential equations which are of the second degree and have a general quadratic first integral.

We might find to try other types of first integrals. Let us mention one simple, still interesting result.

Statement 1 Among the polynomial differential equations of the form

$$\begin{aligned} x' &= ax^2 + bxy + cy^2 + dx + ey + f \\ y' &= Ax^2 + Bxy + Cy^2 + Dx + Ey + F \end{aligned} \tag{30}$$

(defined in the positive quadrant) the only one having

$$V(p,q) := p + q - \ln(p) - \ln(q)$$

as its first integral is

$$x' = bxy - bx \quad y' = -bxy + by, \tag{31}$$

i. e. the Lotka–Volterra equations (allowing possibly time reversal).

Note that the it is not assumed that (30) is a kinetic differential equation, and in the result no restriction is made on the sign of b.

This result is very similar to the result leading uniquely to the Lotka–Volterra model under different circumstances [12,13,19,21,23,34,37].

One might try to generalize this result to the multidimensional case.

Another form of interesting first integrals is a free energy like function:

$$V(\mathbf{c}) := \sum_{m=1}^{M} c_m \ln\left(\frac{c_m}{c_m^0}\right),$$

which turned out to be a useful Lyapunov function for broad classes of reactions [15,39]. Gonzalez-Gascon and Salas [10] have systematically found this type of first integrals (and other types, as well) for three dimensional Lotka–Volterra systems.

The question arises if these first integrals are kept by some numerical methods or not.

5.2 Relations to numerical methods

Even the simplest kinetic differential equations can only be solved by numerical methods, therefore the question if such a method is able to keep important qualitative properties of the models arouse very early [1,7]. The first positive answers included numerical methods which keep the property of kinetic differential equations that starting from a nonnegative initial concentration they provide solutions which are nonnegative throughout their total domain of existence [7,16]. Similarly, numerical methods were constructed to keep linear and quadratic first integrals. The meaning and existence of linear first integrals have been studied in detail: they usually represent mass conservation. The existence of a positive linear first integral together with nonnegativity [38,39] of the solutions implies that the complete solution of the kinetic differential equation is defined on the whole real line, which is not necessarily the case for systems that are not mass conserving. However, quadratic first integrals were almost neglected.

We have always used global first integrals. Another approach is given by Gonzalez-Gascon and Salas [10] who started from local first integrals and tried to extend them in cases if it was possible.

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