

Numerical Stability of EKF-Based Software Sensors in Chemical Engineering: A Van Der Vusse Reaction Case Study

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Abstract—This paper aims at exploring numerical stability properties of various software sensors used in chemical science and engineering. These are applied commonly to evaluation of variables and/or parameters of chemical systems, which cannot be measured by technical means. Practical software sensors are often grounded in the extended Kalman filtering (EKF) method applied to estimation of this and that stochastic model. Usually, a conventional chemical system consists of an Itô-type stochastic differential equation representing the chemical reaction's dynamics and a discrete-time equation linking the model's state to the measurement information. The focus of this research is on the numerical stability of various EKF-based software sensors in the presence of round-off errors. Our case study exploration is fulfilled on the famous Van der Vusse reaction model but used with an ill-conditioned measurement function, here. We reveal that only square-root versions of the EKF-based software sensors (grounded in numerically stable orthogonal transformations) are the methods of choice for state and/or parameter estimations of stochastic chemical systems in the presence of round-off and other disturbances.

Index Terms—continuous-discrete stochastic system, Van der Vusse reaction model, ill-conditioned measurement function, extended Kalman filter

I. INTRODUCTION

It is commonly accepted in applied science and engineering studies that a chemical state estimation task is set for a continuous-discrete stochastic system of the form [1]:

$$dx(t) = F(x(t), u(t))dt + Gdw(t), \quad t > 0, \quad (1)$$

$$y_k = h(x_k) + v_k, \quad k \geq 1. \quad (2)$$

In the above stochastic system, the process equation (1) is justified by the continuous-time fashion of chemical reaction modeling and is usually given as a standard Itô-type *Stochastic Differential Equation* (SDE). Here, the n_1 -dimensional vector $x(t) \in \mathbb{R}^{n_1}$ represents the chemical reaction's state at time t , the n_2 -dimensional vector $u(t) \in \mathbb{R}^{n_2}$ refers to its measurable input at time t and may include control inputs as well, $F: \mathbb{R}^{n_1} \times \mathbb{R}^{n_2} \rightarrow \mathbb{R}^{n_1}$ is a drift function, which describes

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the chemical reaction's kinetics itself, and the time-invariant diffusion matrix G of size $n_1 \times q$ and the zero-mean white Gaussian process $\{w(t), t > 0\}$ with a square covariance matrix $Q > 0$ of size q simulate random disturbances existing in real-world chemical processes. We recall that the notation $Q > 0$ implies the positive definiteness of the matrix Q . The initial state x_0 of SDE (1) also represents a random variable distributed as follows: $x_0 \sim \mathcal{N}(\bar{x}_0, \Pi_0)$ with $\Pi_0 > 0$. Here and below, the notation $\mathcal{N}(\bar{x}_0, \Pi_0)$ refers to the normal distribution with mean \bar{x}_0 and covariance Π_0 .

In the discrete-time measurement equation (2), the subscript k means a discrete time index (i.e. x_k stands for $x(t_k)$), the m -dimensional vector $y_k \in \mathbb{R}^m$ implies the measurement information available at the sampling time t_k , the function $h: \mathbb{R}^{n_1} \rightarrow \mathbb{R}^m$ links the model's state x_k to the measurement information y_k and it is supposed to be differentiable. Lastly, random disturbances of the measurement process are simulated by a Gaussian white-noise sequence $\{v_k, k \geq 1\}$ distributed with zero mean and some covariance matrices $R_k > 0$ in the stochastic model (2) at sampling instants t_k . We assume that the measurement samples arrive uniformly and with the sampling rate $\delta = t_k - t_{k-1}$. Most importantly, all random processes in the stochastic system (1), (2) and its initial state are supposed to be mutually independent.

The main question of the state estimation task stated in chemistry research sounds as follows: With use of the mathematical model (1), (2) and measurement information y_k available at a sampling time t_k , one has to evaluate true values of the chemical reaction quantities x_k , which may not be measured by technical devices (or whose measurement is too expensive in practice). A conventional solution to this task is given in the form of state estimator, which represents a mathematical method (filtering algorithm). It serves for estimation of the continuous-discrete stochastic system at hand. That is why the mentioned filter (presented in the form of a software code) is also interpreted as a *Software Sensor* (SS) [2].

Performance of every SS utilized in chemical engineering studies is fully determined by the objective criterion underlying a particular filter. Below, we consider the *Extended Kalman*

TABLE I
INITIAL VALUES IN OUR ILL-CONDITIONED VAN DER VUSSE REACTION
SCENARIO

state variable	value
c_A	2.1404 mol/L
c_B	1.0903 mol/L
T	387.34 K
T_J	386.06 K

Filtering (EKF) approach, which is the *minimum-variance* technique used commonly for practical state estimation needs in stochastic systems with Gaussian noise. The latter state estimation tasks often arise in various areas of applied science and engineering.

Our study aims at exploration of the numerical robustness and accuracy of EKF-based SS's when these are applied to continuous-time stochastic models of the form (1) but with ill-conditioned discrete-time measurements (2). The high sensitivity of the classical *Kalman Filtering* (KF) method to round-off operations existing in any finite-precision computer arithmetic has been known for long time and investigated extensively in literature (see, for example, [3], [4] and references therein). The cited literature establishes that one potential solution to this ill-conditioning problem lies in the realm of square-root Kalman filtering.

Despite a good deal of sound papers related to numerical robustness investigations of various versions of the KF method, just a little interest has been paid to the continuous-time filtering so far, especially in the context of estimating continuous-discrete stochastic systems of the form (1), (2) in chemical engineering. So, the present exploration bridges this gap by means of the case study investigation of numerical robustness properties of several EKF-based SS's within a stochastic scenario based on the well-known Van der Vusse reaction. We point out that the chosen scenario is a classical benchmark problem in a number of valuable studies in chemistry research, as evidenced, for instance, in [5], [6]. In the next section, we explain how to convert the cited Van der Vusse reaction model into its ill-conditioned variant utilized in our numerical experiments.

II. VAN DER VUSSE REACTION SCENARIO WITH ILL-CONDITIONED MEASUREMENTS

In Sec. II, we follow [6], [7] while presenting the stochastic scenario exploited below. The Van der Vusse reaction under consideration consists of four species marked by the letters A , B , C and D in the cited papers. There, the desired outcome product is B , while C and D are unwanted by-products. This reaction is fulfilled in a *Continuously Stirred Tank Reactor* (CSTR) with a cooling jacket and simulated by the SDE model of the form (1) where the 4-dimensional state vector is $x(t) = (c_A(t), c_B(t), T(t), T_J(t))^T \in \mathbb{R}^4$ with the entries $c_A(t)$ and $c_B(t)$ referring to concentrations of the species A and B at time t and the remaining two $T(t)$ and $T_J(t)$ denoting temperatures of the CSTR and its

TABLE II
FIXED PARAMETERS IN OUR ILL-CONDITIONED VAN DER VUSSE
REACTION SCENARIO

parameter	value
k_{10}	$1.287 \times 10^{+12} \text{ hr}^{-1}$
k_{20}	$1.287 \times 10^{+12} \text{ hr}^{-1}$
k_{30}	$9.043 \times 10^{+9} \text{ L}/(\text{hr} \times \text{mol})$
E_1/R	9758.3 K
E_2/R	9758.3 K
E_3/R	8560 K
ΔH_{r_1}	4.2 kJ/mol
ΔH_{r_2}	-11.0 kJ/mol
ΔH_{r_3}	-41.85 kJ/mol
ρ	0.9342 kg/L
C_p	3.01 kJ/(kg \times K)
k_w	4032 kJ/(hr \times m ² \times K)
A_R	0.215 m ²
V_R	10 L
m_J	5 kg
C_{PJ}	2.0 kJ/(kg \times K)
F	141.9 L/hr
\dot{Q}_J	-1113.5 kJ/hr
c_{A0}	5.1 mol/L
T_0	378.05 K

cooling jacket, respectively. The Van der Vusse reaction's kinetics is simulated by the nonlinear vector-function $F(\cdot) = (f_1(\cdot), f_2(\cdot), f_3(\cdot), f_4(\cdot))^T \in \mathbb{R}^4$ whose entries are presented as follows:

$$\begin{aligned}
 f_1(\cdot) &= \frac{F}{V_R} [c_{A0} - c_A(t)] - k_{10} \exp \left\{ -\frac{E_1}{RT} \right\} c_A(t) \\
 &\quad - k_{30} \exp \left\{ -\frac{E_3}{RT} \right\} c_A^2(t), \\
 f_2(\cdot) &= -\frac{F}{V_R} c_B(t) + k_{10} \exp \left\{ -\frac{E_1}{RT} \right\} c_A(t) \\
 &\quad - k_{20} \exp \left\{ -\frac{E_2}{RT} \right\} c_B(t), \\
 f_3(\cdot) &= \frac{F}{V_R} [T_0 - T'(t)] + \frac{k_w A_R}{\rho C_p V_R} [T_J(t) - T(t)] \\
 &\quad - \left[k_{10} \Delta H_{r_1} \exp \left\{ -\frac{E_1}{RT} \right\} c_A(t) \right. \\
 &\quad \left. + k_{20} \Delta H_{r_2} \exp \left\{ -\frac{E_2}{RT} \right\} c_B(t) \right. \\
 &\quad \left. + k_{30} \Delta H_{r_3} \exp \left\{ -\frac{E_3}{RT} \right\} c_A^2(t) \right] / [\rho C_p], \\
 f_4(\cdot) &= \frac{1}{m_J C_{PJ}} \left(\dot{Q}_J + k_w A_R [T(t) - T_J(t)] \right). \quad (3)
 \end{aligned}$$

The steady-state of our ill-conditioned stochastic scenario (termed the nominal operating point of the Van der Vusse reaction) and its fixed parameters are taken from [6], [7] and presented for convenience in Tables I and II, respectively. In other words, the initial state of SDE (1) is given in Table I. It is used for simulation of reference stochastic solutions and "true"

measurements in Sec. IV. The random disturbance is then modeled by the term $Gw(t)$, which consists of the diagonal diffusion matrix $G = \text{diag}\{2.1404, 1.0903, 387.34, 386.06\}$ and the 4-dimensional standard Brownian motion $w(t)$ with zero mean and identity matrix covariance.

Following [6]–[8], we examine the capacity of several EKF-based SS's for estimating the Van der Vusse reaction's state by means of temperature measurements, only. However, in contrast to the cited papers, our measurement equation is supposed to be ill-conditioned and given by the formula

$$y_k = \begin{pmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 + \sigma \end{pmatrix} x_k + v_k \quad (4)$$

where the vector x_k denotes an approximation to the reaction's state $x(t_k)$ at time t_k , the measurement noise is $v_k \sim \mathcal{N}(0, R_k)$ with the covariance matrix $R_k = \sigma^2 I_2$, in which I_2 stands for the identity matrix of size 2, and σ refers to a small positive real number, which serves for provoking ill-conditioning in our Van der Vusse reaction scenario, i.e. the measurement model (4) becomes increasingly ill-conditioned as $\sigma \rightarrow 0$. Measurements of the form (4) are a typical means in numerical stability explorations of KFs [4].

The stochastic Van der Vusse reaction scenario presented in Sec. II assumes that the fixed parameter c_{A0} in Table II doubles at time $t = 60$ hr, as that done in [7], [8]. The total simulation interval is taken to be $[0, 120 \text{ hr}]$ in our case study.

III. EKF-BASED SOFTWARE SENSORS

In Sec. III, we outline briefly state estimators, which are examined within our ill-conditioned stochastic Van der Vusse reaction scenario. All such filters are built with use of the so-called *continuous-discrete* approach [9]. The principal idea behind all the methods under consideration is to employ the following *Moment Differential Equations* (MDEs):

$$\hat{x}'(t) = F(\hat{x}(t), u(t)), \quad (5)$$

$$P'(t) = J(\hat{x}(t), u(t))P(t) + P(t)J^\top(\hat{x}(t), u(t)) + GQG^\top \quad (6)$$

where the prime denotes the derivative of the corresponding vector (or matrix) with respect to time, for predicting the mean and covariance in each sampling interval of the above scenario. In MDEs (5), (6), the matrix $J(\hat{x}(t), u(t)) = \partial F(\hat{x}(t), u(t)) / \partial \hat{x}(t)$ denotes the Jacobian of the drift coefficient $F(\hat{x}(t), u(t))$, whose entries are defined in formulas (3), the matrix G is also explained in Sec. II, $Q \equiv I_4$ is set here, $\hat{x}(t)$ stands for the mean of the random system's state $x(t)$ at time t (i.e. $x(t)$ is a solution to Eq. (1)), and $u(t)$ is the measurable input, which implies a known function of time.

Having integrated MDEs (5), (6) with the initial values $\hat{x}(t_{k-1}) = \hat{x}_{k-1|k-1}$, $P(t_{k-1}) = P_{k-1|k-1}$, where $\hat{x}_{k-1|k-1}$ and $P_{k-1|k-1}$ refer to the filtering solution calculated at time t_{k-1} , in the sampling interval $[t_{k-1}, t_k]$, one fixes the predicted state expectation and covariance in line with the following rule: $\hat{x}_{k|k-1} = \hat{x}(t_k)$, $P_{k|k-1} = P(t_k)$ where the vector $\hat{x}(t_k)$ and the matrix $P(t_k)$ are numerical solutions to MDEs (5), (6) computed by this or that technique at time t_k . Thus, the diversity of the EKF-based SS's under exploration stems from

the diversity of the numerical integration tools applied. Then, the measurement update step is the standard one in each filter and, hence, it is implemented in line with the following EKF formulas:

$$R_{e,k} = R_k + H_k P_{k|k-1} H_k^\top, \quad K_k = P_{k|k-1} H_k^\top R_{e,k}^{-1}, \quad (7)$$

$$\hat{x}_{k|k} = \hat{x}_{k|k-1} + K_k e_k, \quad e_k = y_k - h(\hat{x}_{k|k-1}), \quad (8)$$

$$P_{k|k} = P_{k|k-1} - K_k H_k P_{k|k-1}, \quad (9)$$

in which the variable Jacobian matrix $H_k = dh(\hat{x}_{k|k-1})/dx_k$ is calculated at the above-predicted state mean $\hat{x}_{k|k-1}$ and $e_k \sim \mathcal{N}(0, R_{e,k})$ are innovations of this method. Finally, the linear least-square estimate $\hat{x}_{k|k}$ of the stochastic Van der Vusse reaction model's state $x(t)$ subject to the derived measurements $\{y_1, \dots, y_k\}$ becomes known at time t_k .

The EKF-based SS (5)–(9) admits a square-root representation as well. The latter preserves automatically the symmetry and positivity of the covariance matrix $P(t)$. Verhaegen and Van Dooren [3] prove that these properties are effective for reducing round-off error accumulations in finite-precision implementations of KFs. One way of obtaining the square-root Kalman filtering relies on the square-root MDEs of the form

$$\hat{x}'(t) = F(\hat{x}(t), u(t)), \quad (10)$$

$$S'(t) = S(t)\Phi(A(t) + A^\top(t) + B(t)). \quad (11)$$

In Eqs (10), (11), the *square root* $S(t)$ stands for the lower triangular matrix in the Cholesky covariance decomposition $P(t) = S(t)S^\top(t)$, $A(t) = S^{-1}(t)J(\hat{x}(t), u(t))S(t)$, $B(t) = S^{-1}(t)GQG^\top S^{-\top}(t)$, and the matrix-function $\Phi(\cdot)$ obeys the formula

$$\Phi_{ij}(M) = \begin{cases} M_{ij}, & \text{if } i > j, \\ M_{ij}/2, & \text{if } i = j, \\ 0, & \text{if } i < j. \end{cases} \quad (12)$$

Here, we have converted the covariance MDE (6) to the square-root one (11) by repeating lines in [1, Appendix]. So, these non-square-root and square-root covariance equations are mathematically equivalent and expected to produce theoretically the same state estimation results in exact arithmetic.

As in the non-square-root EKF-based SS (5)–(9), the square-root MDEs (10)–(12) are to be integrated numerically in the time update step of the square-root Kalman filtering methods outlined below. Again, this time update is grounded in the trivial formulas $\hat{x}_{k|k-1} = \hat{x}(t_k)$ and $S_{k|k-1} = S(t_k)$ at each sampling instant t_k . Then, having received a new measurement y_k and calculated the measurement noise covariance square root $R_k^{1/2}$, i.e. $R_k = R_k^{1/2} R_k^{\top/2}$, the measurement update step is implemented in our square-root filtering techniques as follows:

$$\begin{pmatrix} R_{e,k}^{1/2} & \mathbf{0} \\ \bar{K}_k & S_{k|k} \end{pmatrix} = \begin{pmatrix} R_k^{1/2} & H_k S_{k|k-1} \\ \mathbf{0} & S_{k|k-1} \end{pmatrix} \Theta_{k|k}, \quad (13)$$

$$\hat{x}_{k|k} = \hat{x}_{k|k-1} + \bar{K}_k R_{e,k}^{-1/2} e_k, \quad e_k = y_k - h(\hat{x}_{k|k-1}). \quad (14)$$

Formula (13) implies that its left-hand side consists of the lower triangular block $R_{e,k}^{1/2}$, the full submatrix $\bar{K}_k =$

$P_{k|k-1}H_k^\top R_{e,k}^{-\top/2}$, the lower triangular one $S_{k|k}$ and the zero-block $\mathbf{0}$ of proper size. The first two blocks are read off and utilized in computing the filtering state mean $\hat{x}_{k|k}$ by formulas (14). The filtering covariance square root at the sampling time t_k is merely read off in the form of the lower triangular block $S_{k|k}$. Most importantly, the left-hand side in formula (13) is derived by multiplication with an orthogonal matrix $\Theta_{k|k}$.

Below, we list eight EKF-based state estimators and their acronyms, which are employed in the chemical reaction scenario with ill-conditioned measurements described in Sec. II:

- `ode45` is the abbreviation for the EKF-based SS (5)–(9) where MDEs (5), (6) are treated numerically by the MATLAB code `ode45` with options `AbsTol`= 10^{-6} , `RelTol`= 10^{-6} and `MaxStep`= 0.1 (see [10, Sec. 3.2.1] for further details and the entire state estimation algorithm);
- `ode45 (SR)` is the square-root variant of the first filter `ode45`, in which the square-root MDEs (10), (11) are treated numerically by the ODE solver `ode45` with the same options `AbsTol`= 10^{-6} , `RelTol`= 10^{-6} and `MaxStep`= 0.1;
- `NIRK4` is the abbreviation for the EKF-based SS (5)–(9) where MDEs (5), (6) are treated by the hybrid numerical method `NIRK4 (2) M2` with global error control and the global error threshold $\epsilon_g = 10^{-6}$ (see [11] for further details and the entire state estimation algorithm);
- `NIRK4 (SR)` is the square-root variant of the state estimator `NIRK4` implemented by square-rooting the hybrid method `NIRK4 (2) M2` with global error control and the global error threshold $\epsilon_g = 10^{-6}$ (see [12, Sec. IV] for its full algorithmic description);
- `NIRK6` is the abbreviation for the EKF-based SS (5)–(9) where MDEs (5), (6) are integrated by the hybrid numerical method `NIRK6 (4) M2` with global error control and the global error threshold $\epsilon_g = 10^{-6}$ (see [11] for further details and the entire state estimation algorithm);
- `NIRK6 (SR)` is the square-root variant of the state estimator `NIRK6` implemented by square-rooting the hybrid method `NIRK6 (4) M2` with global error control and the global error threshold $\epsilon_g = 10^{-6}$ (see [8, Sec. 2.3] for its full algorithmic description);
- `M2 (2)` is the abbreviation for the EKF-based SS (5)–(9) where MDEs (5), (6) are treated by the hybrid numerical method `M2 (2)` with local error control and the local error threshold $\epsilon_{loc} = 10^{-6}$ designed in [13] (see [10, Sec. 3.2.2] for its implementation details and the entire state estimation algorithm);
- `ESDIRK3 (4)` is the abbreviation for the EKF-based SS (5)–(9) where MDEs (5), (6) are integrated numerically by the embedded Runge-Kutta pair `ESDIRK3 (4)` with local error control and the local error threshold $\epsilon_{loc} = 10^{-6}$ designed in [14] (see [10, Sec. 3.2.3] for its full algorithmic description).

We stress that the EKF-based SS `ESDIRK3 (4)` is implemented in the *non-square-root* form because of the reason

already explained in [10, Sec. 3.2.3].

IV. NUMERICAL STABILITY EXPLORATION

Here, we explore state estimation accuracies of all the filters elaborated in Sec. III when these are applied to the increasingly ill-conditioned stochastic Van der Vusse reaction model presented in Sec. II. We begin with computing its “true” states, i.e. our reference stochastic solution values $x_{ref}(t_k)$. These are yielded numerically by solving the corresponding SDE with the initial values from Table I by the Euler-Maruyama scheme with the small fixed step size equal to 0.0001 hr in the entire modeling interval of 120 hr. Then, we apply the measurement equation (4) and the reference solution values evaluated at sampling instants t_k for simulating “true” measurements y_k in our stochastic Van der Vusse reaction scenario with ill-conditioned measurements. At last, we solve the reverse problem, i.e. given the stochastic chemical system and the measurement history, we apply the EKF-based SS’s listed in Sec. III for calculating the filtering reaction’s states $\hat{x}_{k|k}$ at the sampling instants t_k . The above procedure is repeated 100 times (Monte Carlo runs) for yielding the *Accumulated Root Mean Square Error* (ARMSE) at each sampling rate, which is accepted here to be $\delta = 1, 2, 3, 4, 5, 6, 10$ hr, by the rule

$$\text{ARMSE} = \left(\frac{1}{100K} \sum_{l=1}^{100} \sum_{k=1}^K \sum_{i=1}^4 (x_{ref,i}^i(t_k) - \hat{x}_{k|k,l}^i)^2 \right)^{1/2}.$$

In the above formula, the superscripts stand for the corresponding entries in the reference and estimated state vectors (i.e. i refers to the concentrations c_A , c_B or to the temperatures $T(t)$ and $T_J(t)$ in our ill-conditioned Van der Vusse reaction scenario), the subscript *ref* marks the “true” stochastic solution computed with the Euler-Maruyama discretization method, l distinguishes the particular Monte Carlo run, k indicates the sampling time t_k in use and $K = \lceil 120/\delta \rceil$, where $\lceil \cdot \rceil$ stands for the integer part of the number, means the total number of samples fulfilled for every value of the sampling rate δ in the entire simulation interval $[0, 120]$ hr.

All the EKF-based SS’s listed in Sec. III are implemented in MATLAB and run under identical conditions. The latter implies that they utilize the same initial values, i.e. $\bar{x}_0 = (2.1404, 1.0903, 387.34, 386.06)^\top$ and $\Pi_0 = 10^{-2}I_4$, as well as the same measurement histories and random noise sequences for providing a fair comparison of their state estimation capacities in the increasingly ill-conditioned stochastic Van der Vusse reaction scenario described in Sec. II. The ill-conditioning is taken to be $\sigma = 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}$. The outcome ARMSE’s of all the filters are plotted in Fig 1.

Fig 1(a) says that when $\sigma = 10^{-5}$, i.e. the Van der Vusse scenario is rather well-conditioned, all our EKF-based SS’s estimate equally well and accurately with the single exception of `ESDIRK3 (4)`. The latter SS exposes its slightly larger ARMSE’s on the chemical system at hand. Then, having increased the ill-conditioning to $\sigma = 10^{-6}$ in our chemical scenario we observe the same filters’ behavior in Fig 1(b) as that in Fig 1(a), but with a single exception. The EKF-based

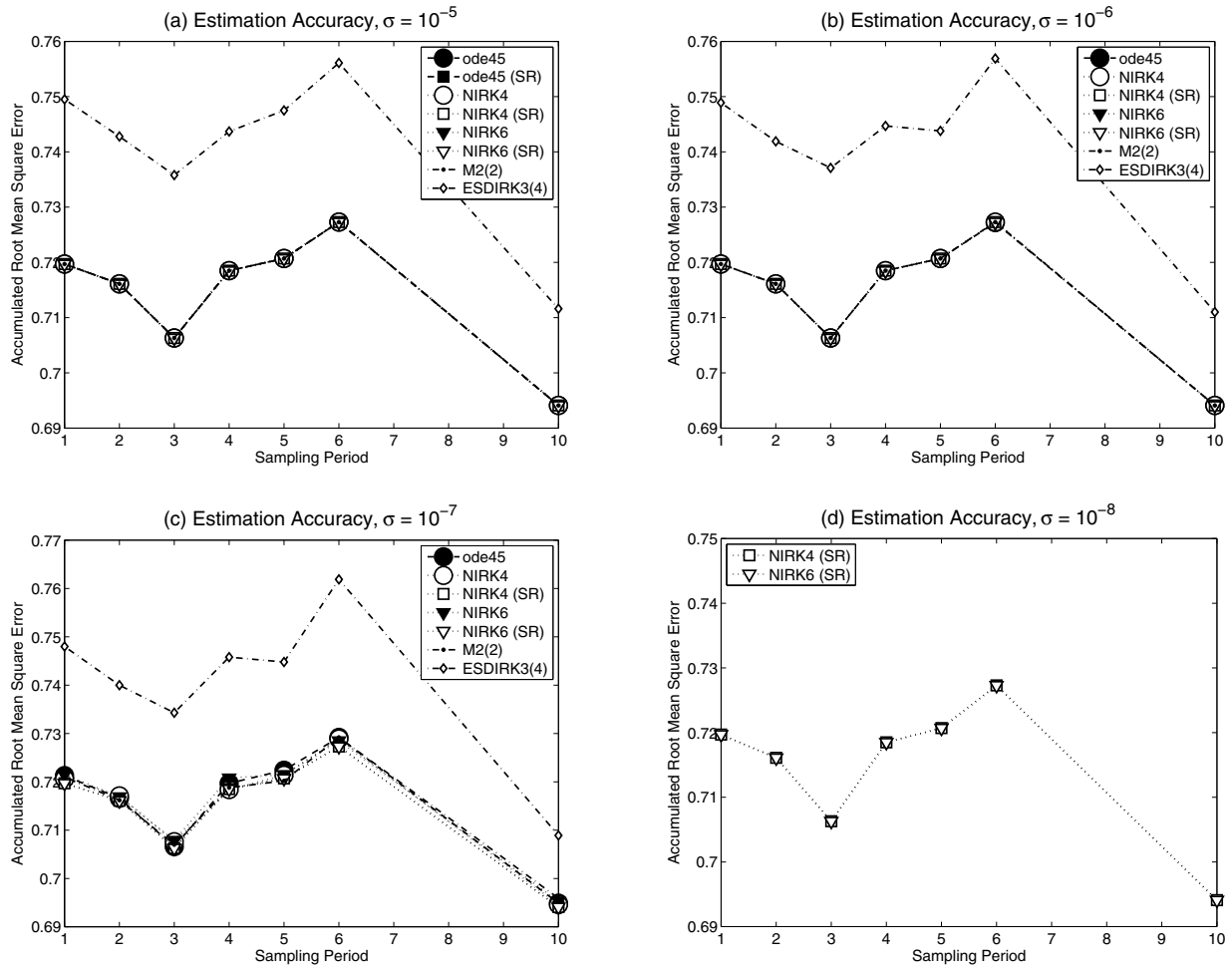


Fig. 1. Filters' accuracies observed within the increasingly ill-conditioned stochastic Van der Vusse reaction scenario

SS ode45 (SR) underperforms the other filters and estimates the reaction's states with the errors exceeding 10. That is why its ARMSE's are not shown in Fig 1(b). The further increase of the ill-conditioning to $\sigma = 10^{-7}$ exposes a similar picture of the filters' behavior in Fig 1(c). However, we see slightly better accuracies achieved with the square-root EKF-based SS's NIRK4 (SR) and NIRK6 (SR) in our case study. Finally, when $\sigma = 10^{-8}$, only the latter two filters are able to estimate successfully this severely ill-conditioned stochastic chemical system. We stress that the square-root methods NIRK4 (SR) and NIRK6 (SR) are equally accurate for all the values of the parameter σ and absolutely insensitive to the increased ill-conditioning in our Van der Vusse reaction scenario. That is why the latter SS's grounded in the stable orthogonal transforms possess the highest numerical robustness to round-off and exhibit the highest state estimation accuracy among the methods listed in Sec. III. Our case study says that these filters are rather promising and can be recommended for practical treatment of various state estimation tasks in chemistry research.

V. CONCLUSION

This paper has examined the numerical stability of EKF-based SS's applicable to stochastic models arisen in chemistry research and engineering. Its focus is on continuous-discrete stochastic systems, in which the chemical reaction kinetics is modeled by means of an Itô-type SDE, but the measurement procedure stays discrete in time. The Van der Vusse reaction model underlies our case study conducted here. To look at the numerical robustness of EKF-based SS's commonly used in practice, when the measurement model becomes increasingly ill-conditioned, we have covered the algorithms grounded in the MATLAB codes as well as in some other MDE solvers designed in the realm of Kalman-like filtering, recently. We have explored the conventional non-square-root methods and also their square-root variants. The square-root SS's have been obtained in two different ways: i) by solving the square-root MDEs (as in the MATLAB-based SS) and ii) by square-rooting the filter itself (as in the NIRK-based methods). Our investigation has revealed that only the square-root filters grounded in the second approach (with use of stable orthogonal transforms) are perfectly stable and allow the highest state estimation

accuracies to be achieved within our stochastic Van der Vusse reaction scenario for various sampling rates. The non-square-root filters and the square-root MATLAB-based SS are found to be rather sensitive to the round-off error accumulation and may be useful and accurate if the chemical system at hand is reasonably well-conditioned. Finally, we have evidenced that NIRK4 (SR) and NIRK6 (SR) are promising techniques for practical treatment of various state estimation tasks in chemistry research.

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