33-767, SS 2019, HW 2 (Feb.-13, 2019)
due: Feb.-20, 2019 (at start of class)

(1) Oscillatory chemical reactions (30 pts)

Oscillatory reactions that are the machinery behind biological clocks based on are by no means limited to “living matter”. There are numerous classical examples of oscillatory chemical reactions such as the Belousov-Zhabotinsky reaction where differently colored reactants visualize spatial and temporal waves in a Petri dish after mixing 5 compounds in water. Here we will analyze such a non-linear reaction.

Assume the following set of reactions which all have negligible back-reactions:

$$A \xrightarrow{k_1} X\,;\; 2X+Y \xrightarrow{k_2} 3X\,;\; B+X \xrightarrow{k_3} Y+C\,;\; X \xrightarrow{k_4} D \qquad (1)$$

Denoting concentrations with lower-case letters, this yields

$$\begin{aligned} \dot{a} &= -k_1 a \\ \dot{b} &= -k_3 bx \\ \dot{c} &= k_3 bx \\ \dot{d} &= k_4 x \end{aligned} \qquad (2) \qquad \text{and} \qquad \begin{aligned} \dot{x} &= k_1 a + k_2 x^2 y - k_3 bx - k_4 x \\ \dot{y} &= -k_2 x^2 y + k_3 bx \end{aligned} \qquad (3)$$

The chemical species of interest are (only) *X* and *Y*. Assume that *A* and *B* are drawn from a large reservoir, such that their concentrations remain approximately constant over the time in which *X* and *Y* show interesting dynamics (a, $b >> x$, y). *C* and *D* do not participate in any forward directions once formed. Their role is to drain concentrations of other compounds. They need not be further considered in a detailed analysis.

With a, b given as constants, one can rescale the relevant Eqns. (3) into dimensionless forms. Define

$$\alpha = \frac{k_1^2 k_2}{k_4^3} a^2\,;\; \beta = \frac{k_3}{k_4} b\,;\; \xi = \frac{k_4}{k_1 a} x\,;\; \eta = \frac{k_4}{k_1 a} y\,;\; \tau = k_4 t \qquad (4)$$

(a) Show that Eqns. (3) can now be rewritten as the following coupled set of nonlinear differential equations:

$$\begin{aligned} \dot{\xi} &= 1 + \alpha \xi^2 \eta - (\beta + 1)\xi \\ \dot{\eta} &= -\alpha \xi^2 \eta + \beta \xi \end{aligned} \qquad (5)$$

The vector $\vec{r} = (\xi, \eta)$ defines a position in a two-dimensional phase space. Rewrite the differential Eqns. (5) in the form $\dot{\vec{r}} = \vec{V}(\vec{r})$ where $\vec{V}(\vec{r})$ is a 2D vector field given by the right-hand eqns. of (5). Explain briefly how the vector field describes the “flow” of $\vec{r}(t)$ in phase space.

(b) A stationary point $\vec{r}_0 = (\xi_0, \eta_0)$ in phase space satisfies $\dot{\xi} = \dot{\eta} = 0$. Find such a stationary point from Eqns. (5) and show that there is exactly one such point.

(c) We need to determine whether $\vec{r}_0$ is stable or not: Do small deviations from $\vec{r}_0$ lead to trajectories that return to $\vec{r}_0$?

For this analysis, expand $\vec{V}(\vec{r})$ around $\vec{r}_0$ up to first order in ξ and η to obtain a linearized matrix close to $\vec{r}_0$:

$$\dot{\vec{r}} \approx \vec{\vec{M}} \cdot (\vec{r} - \vec{r}_0) \tag{6}$$

and find the two eigenvalues $\lambda_{1,2}$ of $\vec{\vec{M}}$. If their real parts are both positive or both negative, then $\vec{r}_0$ is unstable or stable, respectively; if they have opposite sites, you're looking at a saddle point. What is the behavior in that respect of the coupled Eqns. (5) near $\vec{r}_0$, depending on the values of α and β? Under which conditions for α and β do $\lambda_{1,2}$ show imaginary components?

(d) The full behavior of solutions – in particular, conditions that show stable oscillations – cannot be fully evaluated through expansions of $\vec{V}(\vec{r})$ around $\vec{r}_0$, nor can the differential Eqns. (5) be exactly solved. A MATHEMATICA script has the differential equations, the vector field and some initial conditions implemented. Use this script to study the behavior of Eqns. (5) numerically. Choose values for α and β which cover the various possibilities for the structures of the eigenvalues that you have identified. Describe what you find.