Structure-Preserving Numerical Methods for Non-Local Photochemical Kinetics

Mario Pezzella

National Research Council of Italy – Institute for Applied Mathematics Mauro Picone
Member of the Italian INdAM Research group GNCS

Introduction

We present three classes of **high-order structure-preserving** approximation schemes for an integro-differential model describing photochemical reactions.

The Continuous Model

We consider a two-species reaction $\mathtt{A} \xrightarrow{h\nu} \mathtt{B}$ in a conservative setting. Let $c(x,t)$ denote the concentration of $\mathtt{A}$ at time $t \in [0,\mathsf{T}]$ and depth $x \in [0,\mathsf{L}]$. Our model [5] reads

$$\frac{\partial c}{\partial t}(x,t) = -c(x,t)f(x)\int_{\lambda_0}^{\lambda_*}\rho\left(\iota\left(\lambda, C_0(x), \int_0^x c(\xi,t)\,d\xi\right)\right)d\lambda$$

$$\frac{\iota(\cdot)}{I(\lambda)} = \exp\left\{-\mu\left(\varepsilon_{\mathtt{B}}(\lambda)C_0(x)+\varepsilon_{\Delta}(\lambda)\int_0^x c(\xi,t)\,d\xi\right)\right\},$$

where $c^0(x) = c(0,x) > 0$, $C_0(x) = \int_0^L c_0(x)\,dx$ and $\varepsilon_\Delta = \varepsilon_{\mathtt{A}} - \varepsilon_{\mathtt{B}}$ are given. The model incorporates

- **Arrhenius law** $f(x) = \mathcal{A}\exp\left\{-\frac{E_a}{R\,T_K}\right\}e(x)$;
- **Multi-component absorptivities** $\varepsilon_{\mathtt{A}}(\lambda)$ and $\varepsilon_{\mathtt{B}}(\lambda)$;
- **Supra-band-gap** wavelengths $\lambda \in [\lambda_0, \lambda_*]$;
- **Beer-Lambert law** penetration.

We assume that $f \in C^0([0,\mathsf{L}] \to \mathbb{R}_0^+)$, $I \in C^0([\lambda_0,\lambda_*] \to [0,1])$, $\rho \in C^0(\mathbb{R}_0^+ \to \mathbb{R}_0^+)$ are non-negative.

$$c(x,t) > 0, \qquad \forall t \in [0,\mathsf{T}],\ \forall x \in [0,\mathsf{L}],$$
$$c(x,t+\tau) < c(x,t), \qquad \forall t \in [0,\mathsf{T}],\ \forall \tau \in (0,\mathsf{T}-t].$$

We aim to design accurate numerical methods that **preserve these properties for arbitrary stepsizes**.

A NSFD Scheme

A semi-implicit **Non-Standard Finite Difference** (NSFD) [3] discretization of the model yields the method

$$\frac{c_j^{n+1}-c_j^n}{\phi(\Delta t)} = -c_j^{n+1}f(x_j)\Delta\lambda\sum_{l=0}^{N_\lambda-1}\rho\left(\iota\left(\lambda_l, C_0(x_j), \Delta x\sum_{r=0}^{j-1}c_r^n\right)\right)$$

$$\frac{\iota(\cdot)}{I(\lambda_l)} = \exp\left\{-\mu\left(\varepsilon_{\mathtt{B}}(\lambda_l)C_0(x_j)+\varepsilon_\Delta(\lambda_l)\Delta x\sum_{r=0}^{j-1}c_r^n\right)\right\}$$

where $c_j^n \approx c(x_j,t_n)$, with $x_j = j\Delta x$, $t_n = n\Delta t$, and $\lambda_l = \lambda_0 + l\Delta\lambda$ and $\phi: \Delta t \in \mathbb{R}^+ \longrightarrow \phi(\Delta t) = \Delta t + \mathcal{O}(\Delta t^2) \in \mathbb{R}^+$.

Theorem 1.

Independently of $\Delta x, \Delta t, \Delta\lambda \in \mathbb{R}^+$ and for each $j \in \mathbb{N}_0$, the NSFD sequence $\{c_j^n\}_{n\in\mathbb{N}_0}$ is **positive, bounded from above and monotonically decreasing**.

Theorem 2.

Assume that the known functions are continuously differentiable for $x \in [0,\mathsf{L}]$, $t \in [0,\mathsf{T}]$ and $\lambda \in [\lambda_0,\lambda_*]$. Then the NSFD method is **consistent and convergent of order 1**.

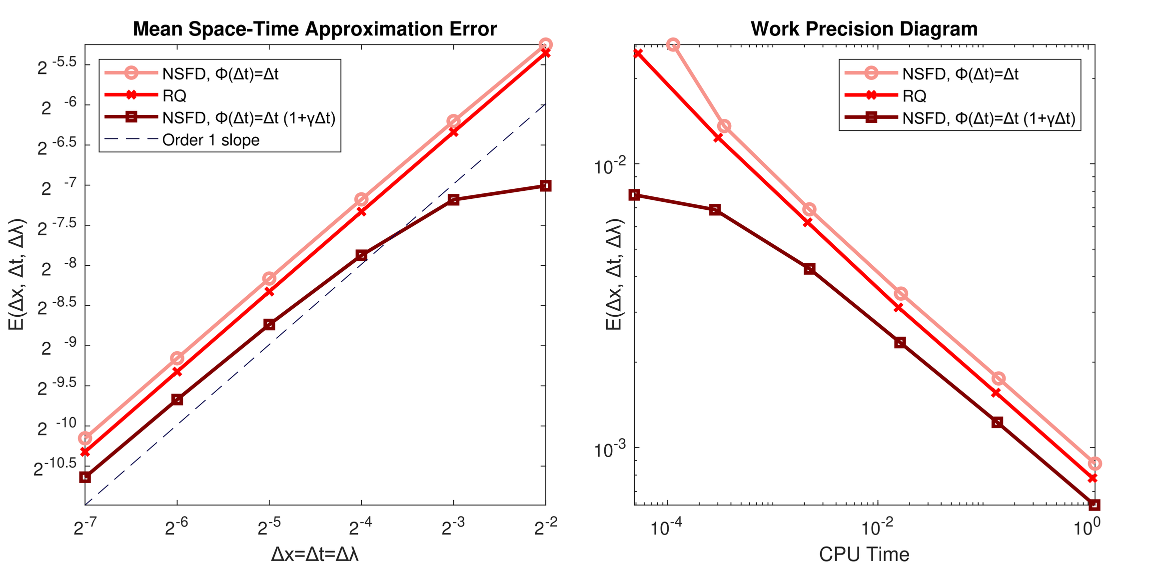

Figure 1: Test Problem 1 from [5]. Here, RQ denotes the Rectangular Quadrature method.

Direct Quadrature Method with Gregory Rules

The model is reformulated as an equivalent **non-linear implicit Volterra integral equation**.
Consider an integer $n_0 \geq 1$. Let $\{w_{\nu\mu}\}$ and $\{\omega_\nu\}$, for $\mu = 0,\dots,n_0-1$ and $\nu \geq n_0$, denote the starting and convolution weights, respectively, of the (n_0-1)-th Gregory quadrature rule [4]. We devise the **Direct Quadrature** (DQ) integrator

$$\log\left(\frac{c_j^n}{c_j^0}\right) = -\Delta t\,\Delta\lambda\, f(x_j)\sum_{p=n_0}^{n}\omega_{n-p}\left\{\sum_{q=0}^{n_0-1} w_{N_\lambda q}\,\rho\left(\iota\left(\lambda_q, C_0(x_j), \Delta x\sum_{k=0}^{n_0-1} w_{jk}c_k^p + \Delta x\sum_{h=n_0}^{j}\omega_{j-h}c_h^p\right)\right) + \sum_{s=n_0}^{N_\lambda}\omega_{N_\lambda-s}\,\rho\left(\iota\left(\lambda_s, C_0(x_j), \Delta x\sum_{k=0}^{n_0-1} w_{jk}c_k^p + \Delta x\sum_{h=n_0}^{j}\omega_{j-h}c_h^p\right)\right)\right\} + \sigma_j$$

$$\iota(\lambda_l,\cdot,\cdot) = I(\lambda_l)\exp\left\{-\mu\left(\varepsilon_{\mathtt{B}}(\lambda_l)C_0(x_j)+\varepsilon_\Delta(\lambda_l)\left(\Delta x\sum_{k=0}^{n_0-1}w_{jk}c_k^p+\Delta x\sum_{h=n_0}^{j}\omega_{j-h}c_h^p\right)\right)\right\}, \qquad l = 0,\dots,N_\lambda,$$

where $c_j^n \approx c(x_j,t_n)$, for $n,j \geq n_0$, the starting values c_k^m, $0 \leq k,m \leq n_0-1$, are given and

$$\sigma_j = -\Delta t\,\Delta\lambda\, f(x_j)\sum_{m=0}^{n_0-1} w_{nm}\left\{\sum_{i=0}^{n_0-1} w_{N_\lambda i}\,\rho\left(\iota\left(\lambda_i, C_0(x_j), \Delta x\sum_{k=0}^{n_0-1}w_{jk}c_k^m+\Delta x\sum_{h=n_0}^{j}\omega_{j-h}c_h^m\right)\right) + \sum_{l=n_0}^{N_\lambda}\omega_{N_\lambda-l}\,\rho\left(\iota\left(\lambda_l, C_0(x_j), \Delta x\sum_{k=0}^{n_0-1}w_{jk}c_k^m+\Delta x\sum_{h=n_0}^{j}\omega_{j-h}c_h^m\right)\right)\right\}.$$

DQ is **fully implicit** by construction $\Longrightarrow$ Well-posedness and **existence of the numerical solution** has to be proven.

- $\mathsf{F}_{\Delta x} = \max_{[0,N_x\Delta x]} f(x)$,
- $W \geq \omega_\nu, w_{\nu\mu}$,
- $\bar{c} = \exp\left\{-\Delta t(N_t+1)\,\Delta\lambda(N_\lambda+1)\,\mathsf{W}^2\,\mathsf{R}\,\mathsf{F}_{\Delta x}\right\}\min_{0\leq j\leq N_x} c_j^0$,
- $\Omega = \left\{[x_0,\dots,x_{N_x}]^T \colon \bar{c}(\Delta x,\Delta t,\Delta\lambda) \leq x_i \leq \max_{0\leq j\leq N_x} c_j^0\right\}$.

Theorem 3.

Let the given initial values satisfy $0 < c_j^m \leq c^0(x_j)$, for $0 \leq m \leq n_0-1$ and $j = 0,\dots,N_x$.
Then, $\forall\,\Delta x, \Delta t, \Delta\lambda \in \mathbb{R}^+$ and $n = n_0,\dots,N_t$, the **DQ non-linear system admits a component-wise positive solution** in $\Omega \subset \mathbb{R}^{N_x+1}$. Furthermore, if $\partial_x f(x_j) \geq 0$ and $\varepsilon_{\mathtt{B}}(\lambda_l) \geq \varepsilon_{\mathtt{A}}(\lambda_l)$, **the solution is unique**.

Theorem 4.

Assume that the known functions are n_0+1 times continuously differentiable. If the starting errors satisfy $|\eta_k^m| = |c(x_k,t_m) - c_k^m| = \mathcal{O}(\Delta x + \Delta t + \Delta\lambda)^{n_0+1}$ for $k = 0,\dots,n_0-1$, and $m = 0,\dots,n_0-1$, then the DQ method is **consistent and convergent of order n_0+1**.

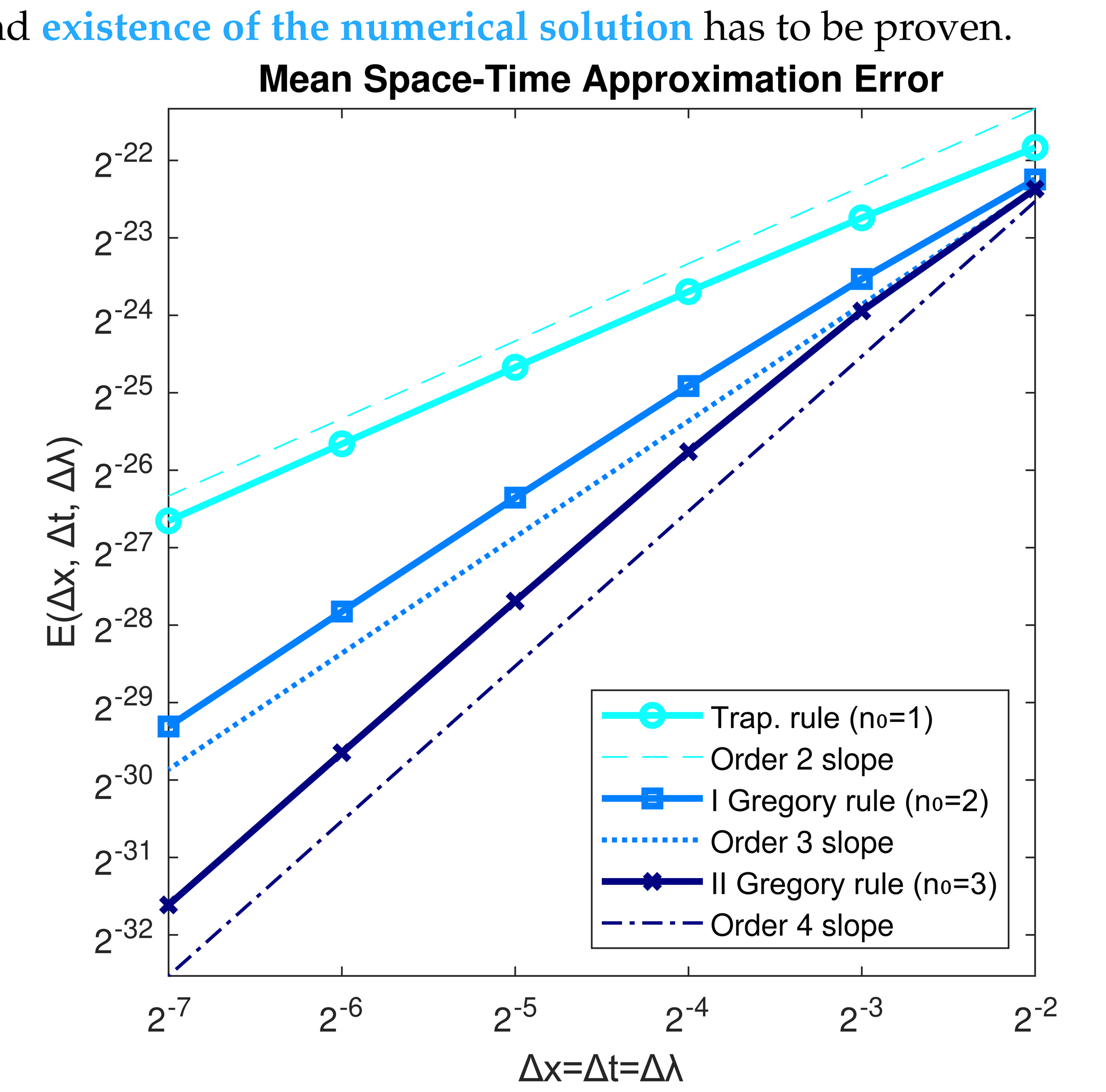

Figure 2: Test Problem 1 from [5], DQ experimental order of convergence.

The DQ methods are **unconditionally positive** and **high order** numerical integrators.

A Predictor-Corrector Approach

We build a **Predictor-Corrector** (PC) method by combining the NSFD approach and the DQ integrator with $n_0 = 1$ and trapezoidal weights.
The PC discretization **inherits the advantages of both discretizations**.

$$\frac{p_j^n}{c_j^{n-1}} = \left\{1+\varphi(\Delta t)\,\Delta\lambda\, f(x_j)\sum_{l=0}^{N_\lambda-1}\rho\left(\iota\left(\lambda_l, C_0(x_j), \Delta x\sum_{r=0}^{j-1}c_r^{n-1}\right)\right)\right\}^{-1},$$

$$\beta_j^l = \rho\left(\iota\left(\lambda_l, C_0(x_j), \frac{\Delta x}{2}\left(c_0^{n-1}+2\sum_{k=1}^{j-1}c_k^{n-1}+c_j^{n-1}\right)\right)\right),$$

$$\gamma_j^l = \rho\left(\iota\left(\lambda_l, C_0(x_j), \frac{\Delta x}{2}\left(p_0^n+2\sum_{k=1}^{j-1}p_k^n+p_j^n\right)\right)\right), \qquad l = 0,\dots,N_\lambda,$$

$$\frac{c_j^n}{c_j^{n-1}} = \exp\left\{-\frac{\Delta t\Delta\lambda}{4}f(x_j)\left(\beta_j^0+\gamma_j^0+2\sum_{l=1}^{N_\lambda-1}(\beta_j^l+\gamma_j^l)+\beta_j^{N_\lambda}+\gamma_j^{N_\lambda}\right)\right\}.$$

Theorem 5.

Independently of $\Delta x, \Delta t, \Delta\lambda \in \mathbb{R}^+$ and for each $j \in \mathbb{N}_0$, the PC sequence $\{c_j^n\}_{n\in\mathbb{N}_0}$ is **positive, bounded from above and monotonically decreasing**.

Theorem 6.

Assume that the known functions are twice continuously differentiable. Then the NSFD method is **consistent and convergent of order 2**.

Applications and Numerical Tests

We model the **release of serotonin** (5-HT) from BHQ-*O*-5HT, a light-sensitive compound used to probe left-right patterning in vertebrate embryos [2].

- $c(x,t)$ is the concentration of BHQ-*O*-5HT at time t and at a distance x from the center of the embryo;
- $c^0(x) = 100\ \mu$M of BHQ-*O*-5HT, microinjected into a single-cell *Xenopus laevis* embryo with a radius $\mathsf{L} = 5.5 \cdot 10^{-2}$ cm.

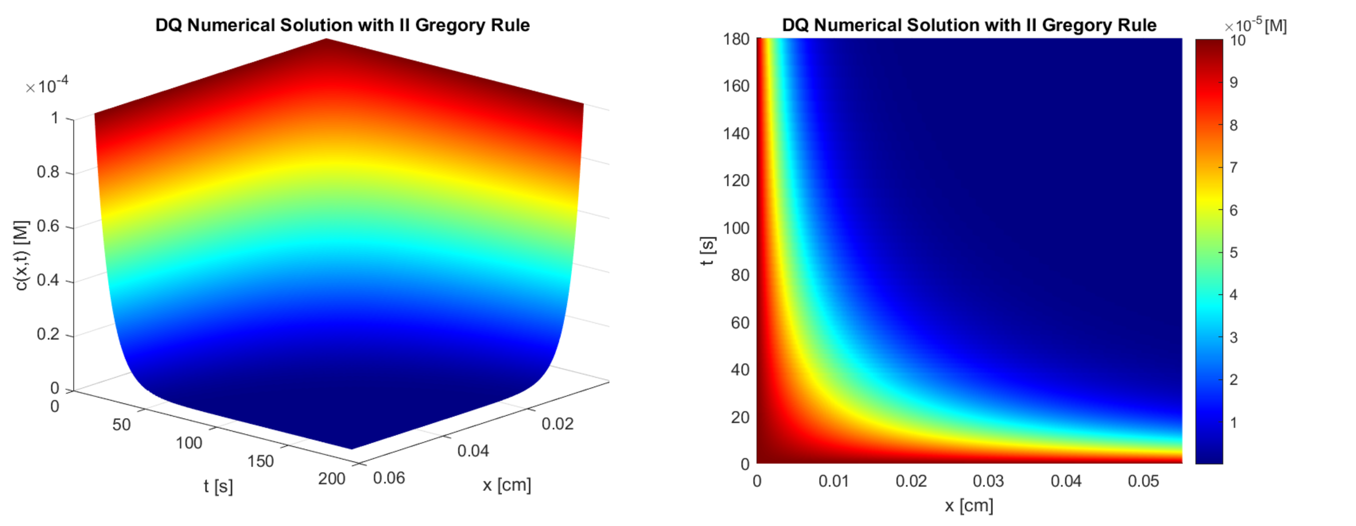

Figure 3: Fourth order simulation of serotonin photoactivation - Test 2 of [5].

We simulate the **photodegradation of cadmium yellow** (CdS), a synthetic pigment widely used in XIX century artworks [1].

$$CdS + 4h_{surf}^{+} + 2H_2O + O_2 \longrightarrow CdSO_4 + 4H^{+}$$

- $c(x,t)$ denotes the CdS concentration at time t and depth x within a painted layer of thickness $\mathsf{L} = 7.00 \cdot 10^{-3}$ cm;
- $c^0(x) = 3.34 \cdot 10^{-2}$ mol cm^{-3} is the initial CdS concentration.

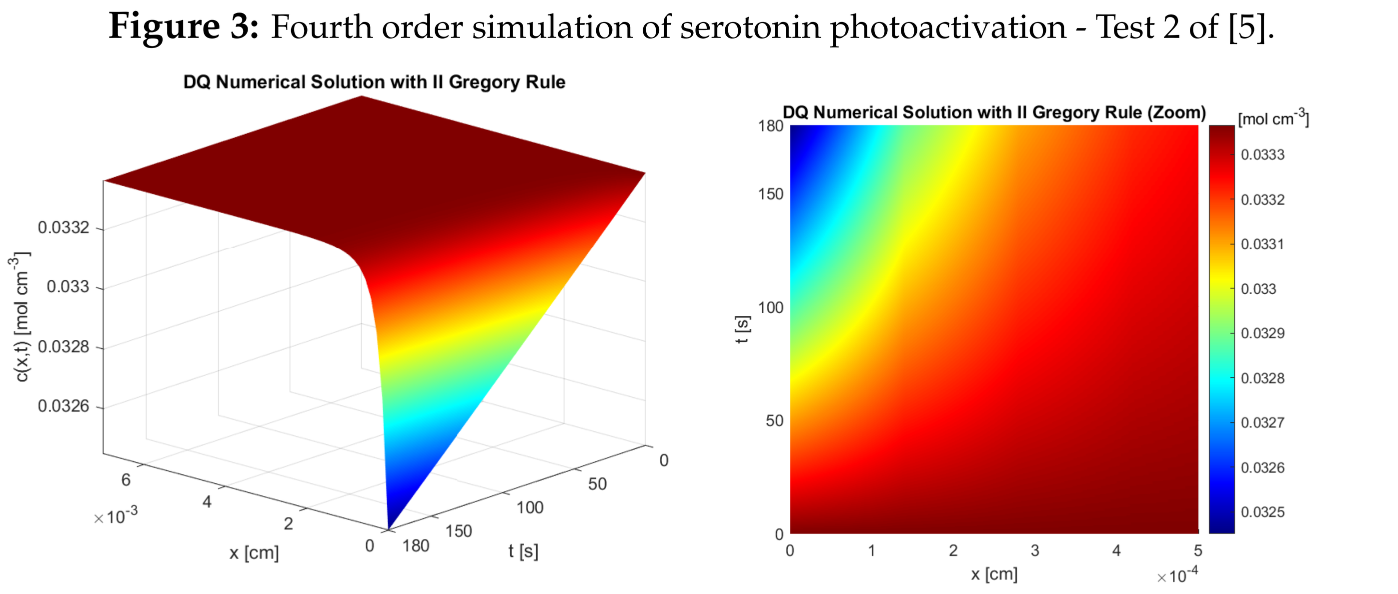

Figure 4: Fourth order simulation of cadmium pigments photodegradation - Test 3 of [5].

References

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