The finite volume method for systems of conservation laws
application to multicomponent mixtures

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The Finite Volume Method for Systems of Conservation Laws

Application to Multicomponent Mixtures

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Summary

Simulating intricate multicomponent mixtures is computationally expensive for mixtures consisting of many species. Moreover, such multicomponent mixtures can have complicated reaction mechanisms and complex diffusion due to coupling between the constituent species. Plasmas can be treated as such a multicomponent mixture, which due to their specific compositions of neutral particles, ions and electrons, add another level of complexity. Consequently, one cannot resolve the behaviour of such mixtures analytically and one has to resort to numerical solutions. However, the complex nature of these mixtures results in coupled conservation laws. The numerical solutions should, therefore, abide the conservation of the quantities in such a system.

Due to this importance of conservation of quantities, the finite volume method (FVM) is employed. FVMs are based on the integral formulation of the conservation law, resulting in a (semi)discrete system involving fluxes. In this thesis novel flux approximation schemes are derived in order to resolve generic one-dimensional conservation laws, both scalar and vectorial, where a linearized reaction term is included in the approximation. Two types of generic conservation laws are considered, first the diffusion-reaction type and second the advection-diffusion-reaction type. The flux approximations are derived following the idea from ten Thije Boonkkamp et al. [1, 2, 3, 4, 5, 6, 7], where the flux is approximated from a local solution of the corresponding boundary value problem. Consequently, the flux approximation is a superposition of a homogeneous flux and an inhomogeneous flux, corresponding to the homogeneous and inhomogeneous solutions of the local boundary value problem. The resulting schemes only have a three-point coupling in one dimension.

The performance of the flux approximation schemes is tested for several problems. For conservation laws of diffusion-reaction type the schemes exhibit uniform second order convergence for the tested diffusive Damköhler numbers. Moreover, the accuracy of the scheme is higher compared to the standard central difference scheme. When simulating multicomponent mixtures the system variant of the scheme still displays second order convergence and increased accuracy compared to the system variant of the standard central difference scheme, when reactions are important. The numerical solutions also show mass and charge conservation up to machine precision without discretisation error.

For conservation laws of advection-diffusion-reaction type the schemes display uniform second order convergence for the tested Péclet and diffusive Damköhler numbers. The accuracy can in several cases be one to two orders of magnitude higher compared to the advection-diffusion schemes presented in [1, 2]. Furthermore, when simulating multicomponent mixtures the system variant of the scheme exhibit second order convergence and increased accuracy compared to the system variant of the advection-diffusion scheme [1], whilst having mass and charge conservation up to machine accuracy without discretisation error. The novel scheme can compute the numerical solution up to the same accuracy, compared to the advection-diffusion variant, using fewer gridpoints.
Preface

The work in this thesis has been completed in a one-year Master of Science-project. The project started on May 16 2018 in the group Elementary Processes in Gas Discharges (EPG) at the department Applied Physics, under supervision of dr.ir. J. (Jan) van Dijk and dr.ir. J.H.M. (Jan) ten Thije Boonkkamp (department of Mathematics and Computer Science). In this project the focus is on deriving novel flux approximation schemes by including a linearized reaction term in the flux approximation, and testing the performances of these schemes. The overall goal of deriving these schemes is to apply them to simulate multicomponent mixtures, and in particular plasmas, efficiently.

These multicomponent mixtures are described by coupled conservation laws. Therefore, taking coupling into account in the flux approximation is rather important. In [1] by ten Thije Boonkkamp et al. this was already done for systems of advection-diffusion type conservation laws, resulting in so-called advection-diffusion complete flux schemes. In this work the idea of computing the flux approximation from a local solution of the boundary value problem, as was done in [1], is also applied to compute flux approximations for schemes where a linearized reaction term is included. The inclusion of the linearized reaction term leads to two variants of conservation laws that can be considered, i.e., the diffusion-reaction type and the advection-diffusion-reaction type. The former is the topic of chapter 3 and the latter is discussed in chapter 4.

At the start of my project, Jan ten Thije Boonkkamp had already derived an expression for the numerical flux vector describing a homogeneous system of diffusion-reaction equations. This was used as a basis for my project. First, an expression for the numerical flux for the homogeneous scalar diffusion-reaction equation was derived. Then, the inhomogeneous flux was computed for both the scalar and system variant. The resulting diffusion-reaction complete flux scheme describes the conservation laws when advection is absent. Next, the generic advection-diffusion-reaction conservation law was considered. This generic advection-diffusion-reaction conservation law resulted in a more complicated derivation of the numerical flux. Luckily, ten Thije Boonkkamp et al. already published a paper for the scalar variant of this problem [7]. In my project, the scalar advection-diffusion-reaction scheme is extended to the system variant of this problem. The first derivation of the homogeneous flux vector is presented in appendix C however, the expression is quite cumbersome. Jan van Dijk suggested to use a different assumption sooner in the derivation, and this lead to the expression of the homogeneous flux described in section 4.2.1. Following that, the inhomogenous flux was derived, resulting in a complete flux scheme for a system of advection-diffusion-reaction equations. In order to test the performance of the flux approximation schemes and simulate mixtures, the full code was written in Python.

Since the goal is to simulate multicomponent mixtures more efficiently using these new schemes, to that purpose the relevant theory of multicomponent mixtures is described in chapter 2. Before the schemes were applied to the complicated multicomponent mixtures, they were tested for various problems that are discussed in chapters 3 and 4. Furthermore, the schemes were applied for two general physics applications in chapter 5. Finally, the schemes were applied to simulate multicomponent mixtures in chapter 6.

Eindhoven, 29 April 2019

Robert van Gestel
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Chapter 1

Introduction

1.1 Conservation laws from continuum physics

In continuum physics conservation laws play a key role, they occur in disciplines like semiconductor physics, fluid mechanics, combustion theory, plasma physics, etc. The conservation laws describe the interplay between transport phenomena, such as advection or drift, diffusion related to a density gradient, and local sources due to chemical reactions or energy absorption from an external heater. These conservation laws can become quite complex due to non-linear terms, for example when considering reacting species. Additionally the conservation laws can be coupled describing an intricate non-linear system of partial differential equations. These conservation laws can be described by a generic coupled system of conservation laws of advection-diffusion-reaction type.

Such a coupled system of conservation laws arises when describing a multicomponent gas mixture. These mixtures have in addition to difficult reaction mechanisms, also a complicated structure of diffusion when no dominant species is present. The diffusion in a multicomponent mixture with no dominant species present, is described by the Stefan-Maxwell equations instead of Fick’s law. The Stefan-Maxwell equations describe that the diffusion of a species is related to all the other species in the mixture, consequently, the conservation laws are coupled through a non-linear diffusion term.

The multicomponent mixtures are governed by conservation laws for mass, momentum and energy for each species. In [8] Peerenboom et al. present how a self-consistent system of conservation laws of advection-diffusion-reaction type for the mass balance can be derived from the Stefan-Maxwell equations. In [9,10] Peerenboom et al. extend this description to describe the mass balance of an ambipolar plasma. The plasma is treated as a multicomponent mixture, where now in addition to mass, momentum and energy balances also a conservation law describing the charge of the mixture must be solved. Due to the presence of charged species, such as positive or negative ions and electrons, in a plasma the interactions within the multicomponent mixture add even more complexities as a result of Coulomb interactions between charged species. And not only the charged species add difficulties, the large mass difference between neutral particles and ions, known as the heavy particles, and electrons results also in rather complicated behaviour. The mass ratio of a heavy particle to an electron is in the order of $10^5$. This mass difference additionally results in a relative high mobility for electrons compared to heavy particles. The mass conservation law for an electron can consequently be advection dominated, while for heavy particles the mass conservation law might be diffusion dominated.

A quasi-neutral plasma consisting of neutrals, electrons and positive ions typically has almost equal particle densities for the electrons and positive ions, i.e., $n_e \approx n_i$ with $n_e$ and $n_i$ the electron and positive ion particle densities, respectively. Moreover, a plasma behaves quite differently from a neutral gas, since a plasma can become electrically conductive due to the charged particles. However, the charge of the charged particles in a plasma can cause an electric field to be generated, which will be diminished by an effect called Debye shielding. The electric field in a plasma will be shielded on
a characteristic length scale called the electron Debye length, which is defined by
\[
\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{n_e e^2}},
\]
where \(\varepsilon_0\) is permittivity of free space, \(k_B\) is the Boltzmann constant and \(e\) is the elementary charge. Furthermore, the Debye length depends on the plasma parameters \(n_e\) and \(T_e\), where the latter is called the electron temperature. On length scales larger than the Debye length, the plasma can be considered quasi-neutral. However, in order to numerically resolve the charges on length scales smaller than the Debye length an excessively fine mesh is required. In the plasmas considered in this thesis, it is more appropriate to consider the electric field in the limit of vanishing Debye length, such that the plasma can be considered quasi-neutral. Another characteristic of a plasma is the ionization fraction defined by
\[
\alpha = \frac{n_e}{n_g + n_e},
\]
where \(n_g\) is the neutral gas density of the plasma. For low pressure plasmas the ionization fraction is typically \(10^{-6}\) to \(10^{-3}\).

Simulating the conservation laws of a plasma or, in general, a multicomponent mixture and taking into account all the complexities can thus be a complicated task. To that purpose we define a model equation, both scalar and vectorial, of advection-diffusion type or advection-diffusion-reaction type. The one-dimensional vectorial conservation law of a generic advection-diffusion-reaction type for the vector of unknowns \(\varphi\) reads
\[
\frac{\partial \varphi}{\partial t} + \frac{\partial}{\partial x} \left( U \varphi - \varepsilon \frac{\partial \varphi}{\partial x} \right) = C \varphi + s,
\]
where \(U\) is the advection matrix, \(\varepsilon = (\varepsilon_{ij})\) is the diffusion matrix and \(C \varphi + s\) represents the complete source term with \(C \varphi\) the linear part of the source term. Throughout this thesis we will refer to equation (1.1.3) as a system of conservation laws of advection-diffusion-reaction type, where \textit{reaction} denotes the linearized source term \(C \varphi\) in the equation. The linear part of the source term can have multiple origins, for example from a linearization of a non-linear source term \[11\]. But also from the source term of reacting species, since the production of the species is at least linear with the species’ density.

### 1.2 Dimensionless parameters

The system (1.1.3) describes the interplay between advection, diffusion and reaction. The interplay between these terms can be described using dimensionless parameters. Consider the scalar stationary one-dimensional conservation law of advection-diffusion-reaction type with constant coefficients given by
\[
\frac{d}{dx} \left( u \varphi - \varepsilon \frac{d \varphi}{dx} \right) = c \varphi + s,
\]
where \(\varphi\) is the unknown variable of interest, \(u\) is the advection coefficient, \(\varepsilon\) the diffusion coefficient and \(c \varphi + s\) the complete source term with \(c \varphi\) the linear part of the source term. By using a characteristic length scale \(L\), the conservation law (1.2.1) can be written as
\[
\text{Pe} \frac{d \varphi}{dx} - \frac{d^2 \varphi}{dx^2} = \text{Da}^d \varphi + \tilde{s},
\]
where \(x = \hat{x}/L\) is the dimensionless length and \(\tilde{s} = \varepsilon^{-1} L^2 s\). Here, we have introduced the Péclet and diffusive Damköhler numbers
\[
\text{Pe} := \frac{u}{\varepsilon} L, \quad (1.2.3)
\]
\[
\text{Da}^d := \frac{c}{\varepsilon} L^2. \quad (1.2.4)
\]
1.3. Finite volume methods

The Péclet number \( \text{Pe} \) expresses the ratio between advective and diffusive transport. When, \( |\text{Pe}| \ll 1 \) diffusion is dominant, while if \( |\text{Pe}| \gg 1 \) advection is dominant. The diffusive Damköhler number \( \text{Da}^d \) instead expresses the ratio between reaction and diffusion. When \( |\text{Da}^d| \ll 1 \) diffusion is dominant, while if \( |\text{Da}^d| \gg 1 \) reaction is dominant and thus local reaction and source balances become more important rather than diffusive transport for determining the unknown \( \varphi(x) \). The Péclet and diffusive Damköhler numbers can also be combined to describe a convective (advective) Damköhler number:

\[
\text{Da}^c := \frac{c}{u} \frac{L}{\text{Pe}}, \quad u \neq 0.
\] (1.2.5)

The convective Damköhler number \( \text{Da}^c \) expresses the ratio between reaction and advection, which is appropriate to use instead of the diffusive Damköhler number when the Péclet number is large.

If a vector of unknowns \( \varphi \) has to be considered, then the stationary variant of (1.1.3) reads

\[
\frac{d}{dx} \left( U \varphi - \mathcal{E} \frac{d\varphi}{dx} \right) = C\varphi + s.
\] (1.2.6)

Next, assume that the coefficient matrices are constant and that the diffusion matrix \( \mathcal{E} \) is regular, which will be shown for a multicomponent mixture in chapter [2]. Then, by utilizing the characteristic length scale \( L \), the system of conservation laws can be written as

\[
\text{Pe} \frac{d\varphi}{dx} - \frac{d^2\varphi}{dx^2} = \text{Da}^d \varphi + \tilde{s},
\] (1.2.7)

where we have introduced \( \tilde{s} := \mathcal{E}^{-1} sL^2 \). The scalar Péclet and Damköhler numbers are replaced by their matrix variants. The Péclet and diffusive Damköhler matrices are given by

\[
\text{Pe} := \mathcal{E}^{-1} U L, \quad \text{Da}^d := \mathcal{E}^{-1} C L^2.
\] (1.2.8)

The Péclet and diffusive Damköhler matrices generalize their scalar variants. The eigenvalues of these matrices then describe whether a linear combination of the unknowns \( \varphi \), described by the corresponding (generalized) eigenvector, is advection, diffusion or reaction dominant.

1.3 Finite volume methods

For multicomponent mixtures the system of conservation laws (1.1.3) is non-linear in the diffusion matrix and reactions. In general, such a system cannot be solved analytically and, therefore, an approximated solution should be obtained using a numerical scheme, which obviously should respect the physical aspects of the system. In this thesis we focus on the space discretisation of conservation laws, both scalar and vectorial, of advection-diffusion-reaction type. For space discretisation several options are available such as finite difference, finite element, finite volume or spectral methods. Due to the importance of conservation of the quantities in our system, we employ the finite volume method.

Finite volume methods are based on the integral formulation of the conservation law, i.e., the conservation law is integrated over a disjunct set of control volumes covering the domain \([1]\). This results in a (semi)discrete system involving fluxes at the interfaces of the control volumes, which need to be approximated. The flux approximations for advection-diffusion type conservation laws were already derived by ten Thijke Boonkamp et al., both scalar \([2]\) and vectorial \([1]\). Furthermore, the numerical schemes presented in those papers were also extended to time dependent problems.
Consider the following generic stationary one-dimensional vectorial conservation law of advection-diffusion-reaction type:

\[
\frac{d}{dx} \left( \mathbf{U} \varphi - \mathbf{E} \frac{d \varphi}{dx} \right) = C \varphi + s(\varphi),
\]

(1.3.1)

which is the stationary variant of equation (1.1.3) with the dependence of \( s = s(\varphi) \) explicitly denoted. Then, the discrete system is obtained by integrating this system over an interval \([\alpha, \beta]\):

\[
\int_{\alpha}^{\beta} (C \varphi + s(\varphi)) \, dx,
\]

(1.3.2a)

with the flux vector \( \mathbf{f}(x) \) defined by

\[
\mathbf{f}(x) = \mathbf{U} \varphi - \mathbf{E} \frac{d \varphi}{dx}.
\]

(1.3.2b)

Next, the domain is covered by a disjunct set of control volumes \( I_j \) of size \( \Delta x \). In this thesis only uniform grids are considered, however, the presented schemes can easily be extended to nonuniform grids. First, we choose the grid points \( x_j \) where the variable \( \varphi \) has to be approximated. Second, we impose the integral form (1.3.2) on a control volume \( I_j := [x_{j-1/2}, x_{j+1/2}] \) with \( x_{j \pm 1/2} = \frac{1}{2}(x_j + x_{j \pm 1}) \), see figure 1.1 and apply the midpoint rule for the integral. The resulting discrete conservation law reads

\[
F_{j+1/2} - F_{j-1/2} = \Delta x \left( C_j \varphi_j + s_j \right).
\]

(1.3.3)

Here, \( F_{j \pm 1/2} \) is the numerical approximation of the flux \( \mathbf{f}(x_{j \pm 1/2}) \), and we denote \( C_j := C(x_j) \), \( \varphi_j := \varphi(x_j) \) and \( s_j := s(\varphi(x_j)) \). The FVM needs to be completed by expressions for the numerical fluxes. The basic idea of the complete flux schemes [1, 2, 3, 4, 5, 6, 7] is to compute the flux from a local boundary value problem (BVP), taking into account the appropriate transport or reaction terms. In this thesis the local BVP for the system (1.3.1) is considered. Solving this local BVP implies that the numerical flux linearly depends on the unknown \( \varphi \) and the source term \( s \) in the neighbouring points \( x_j \) and \( x_{j+1} \), i.e., we are looking for an expression of the form

\[
F_{j+1/2} = \alpha \varphi_j - \beta \varphi_{j+1} + \Delta x (\gamma s_j + \delta s_{j+1}),
\]

(1.3.4)

where the coefficient matrices \( \alpha, \beta, \) etc., are piecewise constant.

The flux approximations for the most generic system of advection-diffusion-reaction type should in the limiting cases reduce to flux approximations for known schemes, such as the flux approximation for the advection-diffusion system considered in [1] when the linear reaction term \( C = 0 \), with \( 0 \) the zero matrix. Therefore, in this thesis the distinction between the different types of conservation laws...
and their respective flux approximation schemes is considered. Assuming steady-state solutions, the following types of systems can be investigated:

Advection-diffusion-reaction (ADR):
\[
\frac{d}{dx} \left( U\varphi - \mathcal{E} \frac{d\varphi}{dx} \right) = C\varphi + s, \quad (1.3.5)
\]

Advection-diffusion (AD):
\[
\frac{d}{dx} \left( U\varphi - \mathcal{E} \frac{d\varphi}{dx} \right) = s, \quad (1.3.6)
\]

Diffusion-reaction (DR):
\[
- \frac{d}{dx} \left( \mathcal{E} \frac{d\varphi}{dx} \right) = C\varphi + s, \quad (1.3.7)
\]

Advection-reaction (AR):
\[
\frac{d}{dx} (U\varphi) = C\varphi + s, \quad (1.3.8)
\]

Diffusion (D):
\[
- \frac{d}{dx} \left( \mathcal{E} \frac{d\varphi}{dx} \right) = s, \quad (1.3.9)
\]

Advection (A):
\[
\frac{d}{dx} (U\varphi) = s, \quad (1.3.10)
\]

Reaction-only (R):
\[
0 = C\varphi + s. \quad (1.3.11)
\]

For the reaction-only system obviously a finite volume method is not needed, instead a non-linear vectorial solver can be used. The flux approximations for the ADR and DR systems naturally allow for oscillatory solutions due to the \(C\varphi\) term, in contrast to the AD system. The flux approximation for the AD system (1.3.6) is presented in [1].

The ODE systems consist of a homogeneous part, the operator for \(\varphi\), and an inhomogeneous part, corresponding to the source term \(s\). If both parts of the ODE system are considered then the analytical solution \(\varphi(x)\) will be referred to as the complete solution, while if only the homogeneous part of the ODE system is solved for, i.e. \(s = 0\), then the solution will be referred to as the homogeneous solution. Since, the solutions depend on their respective dimensionless parameters, the Péclet and diffusive Damköhler matrices, so will the numerical flux approximations. The scalar variants of these different type of conservation laws are also considered in this thesis.

The computation of the numerical flux vector \(F_{j+1/2}\) for diffusion-reaction type conservation laws will be topic of chapter 3. In these chapters the numerical flux for the system variants take into account the coupling between the individual equations, which is of the utmost importance for the numerical solution to abide the conserved quantities [12]. The computation of the numerical flux for advection-diffusion type conservation laws can be found in [12]. Finally, for diffusion and advection type conservation laws the well-known standard central difference scheme and upwind schemes are recovered. To conclude, an overview of the discretized schemes for each type of conservation law, with their flux balances and numerical flux approximations, is given in appendix A.

1.4 Outline

In this thesis, the focus is on deriving novel flux approximation schemes in order to resolve generic conservation laws, both scalar and vectorial, where a linearized reaction term is included in the approximation. The performance of these schemes is evaluated for various examples. The schemes exhibit second order convergence for the tested Péclet and diffusive Damköhler numbers or matrices. Furthermore, the schemes are applied to simulate multicomponent mixtures where the schemes show mass conservation and charge conservation without discretisation error in addition to second order convergence. Moreover, the schemes are also applicable to other equations from fields outside continuum physics, such as the general Helmholtz equation or scalar and coupled non-linear Schrödinger equations [13].

In chapter 2 the relevant conservation laws for describing a multicomponent mixture are presented. Next, the schemes for diffusion-reaction type conservation laws are derived and the perfor-
mance of these schemes is tested in chapter 3. Then, conservation laws of advection-diffusion-reaction type are considered in chapter 4 where the schemes are again derived and again tested. In chapter 5 the scalar schemes are tested on general physics problems showing the wide applicability of the schemes, and in chapter 6 the system schemes are applied to multicomponent mixtures. Finally, a summary and conclusion is given in chapter 7 and suggestions for future research are made in chapter 8.
Chapter 2

Multicomponent diffusion

A gas mixture can be characterized using various approaches, such as a kinetic approach where the gas is described by a large number of particles which are all in random motion. In this work a fluid description of the mixture is used, where the collective behaviour of a large number of particles is described as the average of the individual particles. Furthermore, the mixture is considered to be a multicomponent mixture consisting of different species. The mixture, therefore, is first described using the relevant physical quantities for each species in section 2.1. These physical quantities can change in time and space, therefore the conservation laws that describe these changes are derived from the Boltzmann equation in section 2.2. Then, the chemical reactions that can occur within a general mixture are described in section 2.3. Next, the description of the Stefan-Maxwell equations and their application to a multicomponent mixture are given in section 2.4. Finally, a summary is given where the different aspects of describing the multicomponent mixture are combined.

2.1 Physical quantities

When considering a multicomponent mixture composed of different species $S_i$, we are interested in the particle number densities $n_i$, the masses $m_i$, velocities $\vec{u}_i$, and temperatures $T_i$. The species’ density fractions are defined by

$$X_i := \frac{n_i}{n}, \quad 0 \leq X_i \leq 1,$$

(2.1.1)

where $n$ is the total particle density of the mixture given by

$$n := \sum_i n_i,$$

(2.1.2)

where the sum is taken over the species $S_i$. The species’ mass densities are defined by $\rho_i := n_i m_i$ and the total mass density of the mixture is given by

$$\rho := \sum_i \rho_i.$$

(2.1.3)

For a species’ mass density $\rho_i$ we introduce the species’ mass fractions as

$$y_i := \frac{\rho_i}{\rho}, \quad 0 \leq y_i \leq 1.$$

(2.1.4)

The mass-averaged velocity field $\bar{\vec{u}}$ of the mixture is defined by

$$\bar{\vec{u}} := \sum_i y_i \vec{u}_i.$$

(2.1.5)
Using this definition we can define the diffusion velocities $\vec{v}_i$ as the species velocities relative to the mass-averaged velocity, i.e.,

$$\vec{v}_i := \vec{u}_i - \vec{u}. \tag{2.1.6}$$

From the ideal gas law the partial pressures $p_i$ of the mixture are given by

$$p_i = n_i k_B T_i, \tag{2.1.7}$$

where $k_B$ is Boltzmann’s constant. The species’ pressure fractions are defined by

$$z_i := \frac{p_i}{p}, \quad 0 \leq z_i \leq 1, \tag{2.1.8}$$

where the total pressure of the mixture is given by

$$p := \sum_i p_i. \tag{2.1.9}$$

From the above definitions it is obvious that when summing the density fractions, mass fractions or pressure fractions over all species $S_i$ the result should be equal to 1. The summation over the mass fractions $y_i$ is important in the numerical simulation of the species and thus the equation

$$\sigma^m := \sum_i y_i = 1, \tag{2.1.10}$$

is known as the mass constraint. In addition to this constraint there is also the mass flux constraint given by

$$\sum_i y_i \vec{v}_i = \vec{0}, \tag{2.1.11}$$

which follows immediately from the definition of the diffusion velocities.

2.2 Conservation laws

The distribution function $f_i(\vec{r}, \vec{w}, t)$ describes the probable amount of a species $S_i$ to be in a certain 6-dimensional space $d\vec{r}d\vec{w}$ with position between $\vec{r}$ and $\vec{r} + d\vec{r}$, and velocity between $\vec{w}$ and $\vec{w} + d\vec{w}$. The velocity $\vec{w}$ is the averaged velocity and is related to a species velocity $\vec{u}_i$ by

$$\vec{w} = \vec{u}_i + \vec{c}_i, \tag{2.2.1}$$

where $\vec{c}_i$ is the peculiar velocity describing the thermal motion of the species. The Boltzmann equation describes the evolution of $f_i$ and is given by

$$\frac{\partial f_i}{\partial t} + \frac{\vec{w}}{m_i} \cdot \nabla_{\vec{r}} f_i + \frac{\vec{F}_i}{m_i} \cdot \nabla_{\vec{w}} f_i = \frac{\partial f_i}{\partial t} \bigg|_{\text{coll}}, \tag{2.2.2}$$

where $\vec{F}_i = \vec{F}_i(\vec{r}, t)$ is the force and $\frac{\partial f_i}{\partial t} \bigg|_{\text{coll}}$ is the collision term for species $S_i$, describing the collisional interactions between multiple species. Here $\nabla_{\vec{r}}$ denotes the gradient in position space, whereas $\nabla_{\vec{w}}$ denotes the gradient in velocity space. The conservation laws can be obtained by multiplying the Boltzmann equation with an observable $\varphi_i(\vec{w})$ and averaging the distribution by integrating over its velocity space. In general any averaged property $\langle \varphi_i \rangle (\vec{r}, t)$ can be computed from

$$\langle \varphi_i \rangle (\vec{r}, t) = \frac{1}{n_i} \int \varphi_i(\vec{w}) f_i(\vec{r}, \vec{w}, t)d\vec{w}, \tag{2.2.3}$$

where the particle density $n_i$ is given by

$$n_i(\vec{r}, t) = \int f_i(\vec{r}, \vec{w}, t)d\vec{w}. \tag{2.2.4}$$
In general the conservation law for the averaged property $\langle \varphi_i \rangle (\vec{r}, t)$ reads [14, p. 194-197]

$$\frac{\partial n_i \langle \varphi_i \rangle}{\partial t} + \nabla \cdot (n_i \langle \vec{w} \varphi_i \rangle) - n_i \left( \frac{\vec{F}_i}{m_i} \cdot \nabla \langle \varphi_i \rangle \right) = \left. \frac{\partial n_i \langle \varphi_i \rangle}{\partial t} \right|_{\text{coll}}. \quad (2.2.5)$$

By definition, the average of the peculiar velocity is $\langle \vec{c}_i \rangle = \vec{0}$.

### 2.2.1 Mass conservation

The mass conservation law is obtained by taking $\varphi_i(\vec{w}) = m_i$. The required averages that appear in (2.2.5) are given by

$$\langle m_i \rangle = m_i, \quad \langle m_i \vec{w} \rangle = m_i \vec{u}_i, \quad \nabla \langle \vec{w} \rangle \langle m_i \rangle = \vec{0}. \quad (2.2.6)$$

The mass conservation law then reads [14, p. 197-198]

$$\frac{\partial n_i m_i}{\partial t} + \nabla \cdot (n_i m_i \vec{u}_i) = m_i \omega_i, \quad (2.2.7)$$

with $\omega_i$ the net production rate of a species $S_i$ defined by

$$\omega_i := \left. \frac{\partial n_i}{\partial t} \right|_{\text{coll}}. \quad (2.2.8)$$

Using the definition of the species’ mass fractions, the mass conservation law for species $S_i$ can be rewritten to

$$\frac{\partial \rho y_i}{\partial t} + \nabla \cdot (\rho y_i \vec{u}_i) = m_i \omega_i. \quad (2.2.9)$$

Upon summation over all species $S_i$ we find the total mass conservation law is given by

$$\frac{\partial \rho \sigma^m}{\partial t} + \nabla \cdot (\rho \sigma^m \vec{u}) = 0. \quad (2.2.10)$$

The net production rate $\omega_i$ describes the production or destruction of species $S_i$ from chemical reactions, therefore no net mass is created and thus $\sum_i m_i m_i = 0$. The total mass conservation law describes the behaviour of the species $\sigma^m$.

### 2.2.2 Charge conservation

The charge conservation law is obtained by taking $\varphi_i(\vec{w}) = q_i$, where $q_i$ is the charge of a species $S_i$. The required averages that appear in (2.2.5) are given by

$$\langle q_i \rangle = q_i, \quad \langle q_i \vec{w} \rangle = q_i \vec{u}_i, \quad \nabla \langle \vec{w} \rangle \langle q_i \rangle = \vec{0}. \quad (2.2.11)$$

The total charge conservation law is found by applying these relations and summing over all species $S_i$, resulting in

$$\frac{\partial \rho \sigma^c}{\partial t} + \nabla \cdot \vec{j} = 0, \quad (2.2.12)$$

Furthermore, the following variables have been defined

$$\sigma^c := \sum_i \frac{q_i}{m_i} y_i, \quad \vec{j} := \sum_i n_i q_i \vec{u}_i, \quad (2.2.13)$$

with $\sigma^c$ the charge conservation species and $\vec{j}$ the current density. Moreover, the charge of the mixtures can be separated into positively and negatively charged particles, i.e.,

$$\sigma^c_+ := \sum_{i,q_i>0} \frac{q_i}{m_i} y_i, \quad \sigma^c_- := \sum_{i,q_i<0} \frac{q_i}{m_i} y_i, \quad (2.2.14)$$
such that
\[ \sigma^c = \sigma^c_u + \sigma^c_c. \]  
(2.2.15)

For a neutral mixture there should be no net charge, therefore we define the charge constraint by
\[ \frac{\sigma^c}{\sigma^c_c} := 0. \]  
(2.2.16)

### 2.2.3 Momentum conservation

The momentum conservation law is obtained by taking \( \varphi_i(\vec{w}) = m_i(\vec{u}_i + \vec{c}_i) \), resulting in
\[ \frac{\partial n_i m_i \vec{u}_i}{\partial t} + \nabla \cdot (n_i m_i \vec{u}_i \vec{u}_i) + \nabla \cdot (n_i m_i \langle \vec{c}_i \vec{c}_i \rangle) - n_i \left\langle \vec{F}_i \right\rangle = \frac{\partial n_i m_i \vec{u}_i}{\partial t} \bigg|_{\text{coll}}, \]  
(2.2.17)

where \( \nabla \vec{w}(m_i \vec{u}) = m_i I \) has been used, with \( I \) the 3 x 3 identity tensor. The momentum conservation law can be rewritten to [14, p. 200-202]
\[ \frac{\partial p_i}{\partial t} + \nabla \cdot (\rho m_i \vec{u} \vec{u}_i) + \nabla \cdot \vec{P}_i - n_i \left\langle \vec{F}_i \right\rangle = \vec{R}_i. \]  
(2.2.18)

Here \( \vec{P}_i \) is the kinetic pressure tensor, which can be rewritten to
\[ \vec{P}_i = p_i I - \bar{\tau}_i, \]  
(2.2.19)

where \( p_i \) is the scalar partial pressure and \( \bar{\tau}_i \) the viscous stress tensor. Furthermore, \( \vec{R}_i \) describes the momentum transfer due to collisional interactions and is given by
\[ \vec{R}_i := \frac{\partial n_i m_i \vec{u}_i}{\partial t} \bigg|_{\text{coll}}. \]  
(2.2.20)

Upon summation over all species \( S_i \) the total momentum conservation law is given by
\[ \frac{\partial \rho \sigma m \vec{u}}{\partial t} + \nabla \cdot (\rho \sigma m \vec{u} \vec{u}) = -\nabla \rho p + \nabla \cdot \bar{\tau} + \sum_i n_i \left\langle \vec{F}_i \right\rangle, \]  
(2.2.21)

which is commonly known as the Navier-Stokes equations.

### 2.2.4 Energy conservation

The energy conservation law is obtained by taking \( \varphi_i(\vec{w}) = \frac{1}{2} m_i (\vec{u}_i + \vec{c}_i) (\vec{u}_i + \vec{c}_i) \), resulting in [14, p. 204-205]
\[ \frac{3}{2} \frac{\partial p_i}{\partial t} + \frac{\partial}{\partial t} \left( \frac{1}{2} n_i m_i u_i^2 \right) + \nabla \cdot \left( \frac{1}{2} n_i m_i \langle w^2 \vec{w} \rangle \right) - n_i \left\langle \vec{F}_i \cdot \vec{w} \right\rangle = Q_i, \]  
(2.2.22)

where \( Q_i \) describes the transfer of energy due to collisional interactions. The third term on the left-hand side can be simplified using
\[ \langle (\vec{w} \cdot \vec{w}) \vec{w} \rangle = u_i^2 \vec{u}_i + \langle c_i^2 \rangle \vec{u}_i + 2 \langle \vec{c}_i \vec{c}_i \rangle \cdot \vec{u}_i + \langle c_i^2 \rangle, \]  
(2.2.23)

and by using the relations
\[ \frac{1}{2} n_i m_i \langle c_i^2 \rangle = \bar{q}_i, \]  
(2.2.24a)
\[ \frac{1}{2} n_i m_i \langle c_i^2 \rangle = \frac{3}{2} \bar{p}_i, \]  
(2.2.24b)
where \( \vec{q}_i \) is the heat flux vector and \( p_i \) is the partial pressure. Using these simplifications the energy conservation law reads
\[
\frac{\partial}{\partial t} \left( \frac{3}{2} p_i + \frac{1}{2} \rho_i y_i u_i^2 \right) + \nabla \cdot \left( \frac{3}{2} \rho_i \vec{u}_i \vec{u}_i + \frac{1}{2} \rho_i y_i u_i^2 \vec{u}_i + (P_i \cdot u_i) + \vec{q}_i \right) - n_i \left( \vec{F}_i \cdot \vec{w} \right) = Q_i. \tag{2.2.25}
\]

The following term can also be rewritten \([14, p. 205-206]\)
\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho_i y_i u_i^2 \right) + \nabla \cdot \left( \frac{1}{2} \rho_i y_i u_i^2 \vec{u}_i \right) = -\frac{1}{2} m_i u_i^2 \omega_i + n_i \vec{u}_i \cdot \left( \vec{F}_i \right) - \vec{u}_i \cdot \left( \nabla \cdot P_i \right) + \vec{u}_i \cdot \vec{R}_i, \tag{2.2.26}
\]

and furthermore the following relation holds
\[
\nabla \cdot (P_i \cdot \vec{u}_i) - \vec{u}_i \cdot (\nabla \cdot P_i) = \nabla \cdot (P_i \cdot \vec{u}_i) - \vec{u}_i \cdot \nabla P_i - (\vec{\tau}_i \cdot \nabla \cdot P_i) \cdot \vec{u}_i. \tag{2.2.27}
\]

Finally, the energy conservation law reads \([15, p. 41]\)
\[
\frac{\partial}{\partial t} \left( \frac{3}{2} p_i \right) + \nabla \cdot \left( \frac{5}{2} \rho_i \vec{u}_i \right) - \vec{u}_i \cdot \nabla \rho p_i - (\vec{\tau}_i \cdot \nabla \rho) \cdot \vec{u}_i + \nabla \cdot \vec{q}_i = n_i \left( \vec{F}_i \cdot \vec{w} \right)
\]
\[
= Q_i - \vec{u}_i \cdot \vec{R}_i + \frac{1}{2} m_i u_i^2 \omega_i, \tag{2.2.28}
\]

where the fourth term on the LHS describes the work done by viscous forces on the system, the fifth term describes the change of energy due to a heat flux, and the terms on the RHS describe the change of energy due to collisional interactions. Moreover, the partial pressure \( p_i \) is related to the temperature by the ideal gas law \( (2.1.7) \).

A plasma consists of electrons and heavy particles, such as ions and neutrals. The behaviour of these species is much different, since the electrons have a much lower mass and higher mobility compared to the heavy particles. Moreover, electrons gain a much larger velocity from an electric field compared to ions, due to their lower mass, and can therefore induce inelastic processes like excitation, ionization and dissociation. Due to the large difference in mass between electrons and heavy particles, the collisional energy transfer can be inefficient. The collisions between heavy particles do not suffer from this large difference in mass, therefore the energy transfer between the heavy particles can be efficient. For these reasons the electron temperature can exceed the heavy particle temperature \([15]\). The energy balances for the heavy particles and electrons are, therefore, considered separately \([15, p. 42]\).

\[
\frac{\partial}{\partial t} \left( \frac{3}{2} n_i k_B T_h \right) + \nabla \cdot \left( \frac{5}{2} n_i k_B T_h \vec{u} \right) - \vec{u} \cdot \nabla p_h - (\vec{\tau} \cdot \nabla \rho) \cdot \vec{u} + \nabla \cdot \vec{q}_h = Q_h, \tag{2.2.29a}
\]
\[
\frac{\partial}{\partial t} \left( \frac{3}{2} n_e k_B T_e \right) + \nabla \cdot \left( \frac{5}{2} n_e k_B T_e \vec{u} \right) - \vec{u} \cdot \nabla p_e + \nabla \cdot \vec{q}_e = Q_e, \tag{2.2.29b}
\]

where the quantities with the \( h \) subscript denote the heavy particle quantity and the \( e \) subscript denote the electron quantity. The viscous dissipation of the electrons is neglected.

The energy balances for the heavy particles and electrons are not considered in this thesis, when simulating the plasma described in chapter 6. Instead the assumption is made that it is a one-temperature plasma, i.e., \( T_h = T_e \).

### 2.3 Reaction source terms

For the mass conservation laws \( (2.2.9) \) the source term \( \omega_i \) describes the chemical reactions in the system. A general reaction \( j \) involving \( N_s \) species can be written as
\[
\sum_{i=1}^{N_s} n_{ij}^i S_i^j \rightarrow \sum_{i=1}^{N_s} n_{ij}^p S_i^p, \quad (2.3.1)
\]
where $\nu_{ij}^d$ and $\nu_{ij}^p$ are the stoichiometric coefficients of the species for destruction and production, respectively. The source term for species $S_i$ can be found by multiplying the net production of species $S_i$ in one reaction event with the reaction rate $Z_j$ of that reaction and summing over the reactions, i.e.,

$$\omega_i := \sum_{j=1}^{N_r} (\nu_{ij}^p - \nu_{ij}^d) Z_j,$$

where $N_r$ denotes the total number of reactions. The volumetric rate of reaction $j$ is given by

$$Z_j(n) := k_j \prod_{i=1}^{N_s} n_i^{\nu_{ij}},$$

where $k_j$ is the rate coefficient of the reaction and $n = (n_1, ..., n_{N_s})^T$ is the particle density vector. The rate coefficient $k_j$ can be described by the general Arrhenius expression

$$k_j(T) = A \left( \frac{T}{T_{ref}} \right)^q e^{-E_a/(RT)},$$

where $A$ is a constant factor for each chemical reaction, the $T_{ref}$ a reference temperature, $q$ an exponential factor, $E_a$ the activation energy for the reaction and $R$ the universal gas constant. The source terms $\omega_i$ can be collected in a vector $\omega$, given by

$$\omega := \nu Z,$$

where $\nu = (\nu_{ij})$ is the stoichiometric matrix with elements $\nu_{ij} = \nu_{ij}^p - \nu_{ij}^d$ and $Z = (Z_j)^T$ is the reaction rate vector. The stoichiometric matrix $\nu$ is an $N_s \times N_r$ matrix and the reaction rate vector $Z$ is represented by a vector with $N_r$ elements. Note that the stoichiometric matrix is always constant.

### 2.4 Stefan-Maxwell equations

In order to solve the mass conservation laws (2.2.9) for a mixture of $m := N_s$ species, we require the species’ velocities $\vec{u}_i$, which can be obtained from the momentum balance equations (2.2.18). However, in practice the species momentum balance equations are not solved for directly, instead the Stefan-Maxwell equations are used for finding the species’ velocities $\vec{u}_i$. The Stefan-Maxwell equations can be derived from the Navier-Stokes equations with certain simplifications [16, p. 219].

The following assumptions are made

- the species’ velocities $\vec{u}_i$ are quasi-steady state;
- diffusive inertial effects are negligible;
- diffusive stresses are negligible;
- viscous effects are negligible;
- reactive terms are negligible.

In this section a summary of the theory presented in [15, 17] is given. First an expression for the diffusive mass fluxes will be derived from the Stefan-Maxwell equations. Then the ordinary diffusion driving force is investigated, followed by an extension of the diffusive mass fluxes to include ambipolar diffusion.
2.4. Stefan-Maxwell equations

2.4.1 Diffusive mass fluxes

In order to elaborate the derivation of the diffusive mass fluxes we rewrite the mass conservation law to

\[ \frac{\partial (\rho y_i)}{\partial t} + \nabla \cdot (\rho y_i \vec{u}) + \nabla \cdot (\rho y_i \vec{v}_i) = m_i \omega_i, \]

(2.4.1)

where the subscript of \( \nabla \) has been dropped. The diffusive velocities \( \vec{v}_i \) are described by the set of Stefan-Maxwell equations, given by

\[ \sum_{j \neq i} \frac{X_i X_j}{D_{ij}} (\vec{v}_i - \vec{v}_j) = -\vec{d}_i, \]

where the sum is taken over the species \( S_j \), and \( D_{ij} \) are binary diffusivities and \( \vec{d}_i \) is the driving force for species \( S_i \). The driving force is given by

\[ \vec{d}_i = \nabla X_i + (X_i - y_i) \frac{\nabla p}{p} + \frac{\rho_i}{p} (\vec{a} - \vec{a}_i), \]

(2.4.2)

where the term \( \nabla X_i \) is due to ordinary diffusion, \( (X_i - y_i) \frac{\nabla p}{p} \) due to pressure diffusion and \( \frac{\rho_i}{p} (\vec{a} - \vec{a}_i) \) due to forced diffusion. The term \( \vec{a}_i \) presents the volume force on species \( S_i \) and \( \vec{a} := \sum_i y_i \vec{a}_i \). In this thesis only one-temperature mixtures are considered. If this is not the case, then the density fractions in the above equations need to be replaced by pressure fractions. For more details see [15].

Next we will use the superscript \( k \) to denote the \( k \)-th spatial coordinate of a vector. Then the Stefan-Maxwell equations can be written as

\[ \sum_{j \neq i} \frac{X_i X_j}{D_{ij}} (\vec{v}^k_i - \vec{v}^k_j) = -\vec{d}^k_i, \quad \forall k \in \{1, 2, 3\}. \]

(2.4.3)

The Stefan-Maxwell equations can also be collected in a matrix-vector product, i.e.,

\[ \mathbf{F} \mathbf{v}^k = -\mathbf{d}^k. \]

(2.4.4)

Here \( \mathbf{F} = (F_{ij}) \) is the friction matrix, with \( F_{ij} \) given by

\[ F_{ij} = \begin{cases} -f_{ij} & \text{if } i \neq j, \\ \sum_{k \neq i} f_{ik} & \text{if } i = j, \end{cases} \]

(2.4.5)

were we have defined the friction coefficients \( f_{ij} \) by

\[ f_{ij} := \frac{X_i X_j}{D_{ij}}, \]

(2.4.6)

which are as mentioned before only valid for one-temperature mixtures.

The diffusion velocities can also be found from

\[ \mathbf{v}^k = -\mathbf{D} \mathbf{d}^k, \]

(2.4.7)

with \( \mathbf{D} \) the symmetric multicomponent diffusion coefficient matrix. The matrix \( \mathbf{D} \), however, cannot be obtained from the inversion of \( \mathbf{F} \) since \( \mathbf{F} \) is singular. Giovangigli [18, p. 78] made use of the nullspace and range of the matrices \( \mathbf{D} \) and \( \mathbf{F} \), and the theory of generalized inverses in order to regularize the matrices. From this regularization the regularized multicomponent diffusion matrix can be found. This regularization essentially adds multiple times the mass-flux constraint (2.1.11) to the system (2.4.4). Consequently, only the mathematical structure of the friction matrix is modified, but not the resulting physical diffusion velocities.
However, this definition is still inadequate in the limit of a vanishing density fraction \( X_i \). The friction matrix \( F \) cannot be regularized in this case. Giovangigli [19, p. 258] suggested to rewrite the set of Stefan-Maxwell equations to

\[
F (\rho \text{diag}(y))^{-1} (\rho \text{diag}(y) v^k) = -d^k,
\]

where \( y = (y_1, \ldots, y_m)^T \) is the vector of mass fractions and \( \text{diag}(y) \) is a diagonal matrix with the elements of the vector \( y \) on the diagonal. This set of Stefan-Maxwell equations (2.4.8) can be written as

\[
H J^k = -d^k,
\]

where \( J^k = \rho \text{diag}(y) v^k \) is the diffusive mass flux vector, with elements \( J^k_i = (\rho y_i v^k_i) \) for each species \( S_i \). Here \( H = F (\rho \text{diag}(y))^{-1} = (H_{ij}) \) is the modified friction matrix, with \( H_{ij} \) given by

\[
H_{ij} = \begin{cases} -h_{ij} & \text{if } i \neq j, \\ \sum_{k \neq j} h_{kj} & \text{if } i = j, \end{cases}
\]

where the modified friction coefficients \( h_{ij} \) are given by

\[
h_{ij} := \frac{m}{\rho m_j D_{ij}} X_i X_j.
\]

Combining the definition of the diffusive mass fluxes and equation (2.4.7) results in

\[
J^k = -L d^k,
\]

where \( L = \rho \text{diag}(y) D \).

The matrix \( H \) is obviously singular, therefore, Giovangigli again made use of the nullspace and range of the matrices \( L \) and \( H \), and the theory of generalized inverses in order to regularize the matrices. The nullspace \( N \) and range \( R \) of the matrices are given by [19, p. 257]

\[
N(H) = N(L) = y, \quad (2.4.13a)
\]

\[
R(H) = R(L) = 1^\perp, \quad (2.4.13b)
\]

where \( 1 = (1, \ldots, 1)^T \) and \( \perp \) denotes the orthoplement of the vector. Regularizing the matrices results in [19, p. 258]

\[
\tilde{H} = H + \alpha y 1^T, \quad (2.4.14a)
\]

\[
\tilde{L} = L + \beta y 1^T. \quad (2.4.14b)
\]

Here \( \alpha \) and \( \beta \) are free positive regularization constants, which are related to each other via

\[
\tilde{H} \tilde{L} = H L + \alpha \beta \sigma^m y 1^T = I - (\sigma^m)^{-1} y 1^T + \alpha \beta \sigma^m y 1^T.
\]

Therefore, if \( \alpha \) and \( \beta \) satisfy \( \alpha \beta (\sigma^m)^2 = 1 \), then the matrices \( \tilde{H} \) and \( \tilde{L} \) are inverses of each other. An appropriate choice for the regularization constant needs to be made, such that the regularization matrix \( \alpha y 1^T \) has the same order of magnitude as the elements of \( H \). Therefore, we use

\[
\alpha = \frac{1}{\rho \max(D_{ij})}. \quad (2.4.16)
\]

Finally, the diffusive mass fluxes are given by

\[
J^k = -\tilde{L} d^k, \quad (2.4.17)
\]

where \( \tilde{L} \) can be found from the regularized modified friction matrix \( \tilde{H} \).
2.4.2 Ordinary diffusion

If only ordinary diffusion is present, i.e. \( \vec{d}_i = \nabla X_i \), then the diffusive mass fluxes (2.4.17) are given by

\[
J^k = - \tilde{L} \frac{\partial}{\partial x^k} X, \quad \forall k \in \{1, 2, 3\}
\]  

(2.4.18)

where \( X = (X_1, ..., X_m)^T \) and \( \frac{\partial}{\partial x^k} \) represents the derivative to a coordinate. The mass balances are written in gradients of the mass fractions \( y \), therefore a conversion matrix \( M \) of the density fractions to mass fractions is needed. However, a straightforward conversion leads to a singular matrix \( M \).

Giovangigli solved the problem by redefining the average mass as [18, eq. (4.4), (4.6)]

\[
m = \frac{\sigma^m}{\sum_i y_i/m_i} = \frac{\sum_i X_i m_i}{\sigma^m},
\]  

(2.4.19)

where \( \sigma^m \) is defined by equation (2.1.10). The regular conversion matrix \( \tilde{M} \) can now be found by taking the derivative of the mass fractions with respect to the density fractions, resulting in

\[
\partial X_i = X_i \sum_j \left( \delta_{ij} + \frac{1}{\sigma^m} (y_j - X_j) \right) y_j^{-1} \partial y_j,
\]  

(2.4.20)

where \( \delta_{ij} \) is the Kronecker delta. The density and mass fractions can be collected in a vector, i.e.,

\[
\partial X = \tilde{M} \partial y,
\]  

(2.4.21)

with

\[
\tilde{M} = \text{diag} (X) \left( I + \frac{1}{\sigma^m} (y - X)^T \right) (\text{diag} (y))^{-1}.
\]  

(2.4.22)

Note that \( 1^T \tilde{M} = 1^T \). Now that we have an expression for the conversion matrix, the diffusive mass fluxes become

\[
J^k = -E \frac{\partial}{\partial x^k} y, \quad \forall k \in \{1, 2, 3\},
\]  

(2.4.23)

where the diffusion matrix \( E \) is given by

\[
E = \tilde{L} \tilde{M}.
\]  

(2.4.24)

Mass conservation for the diffusion matrix can be found if \( 1^T \) is a left eigenvector. Indeed, we find

\[
1^T E = 1^T \tilde{L} \tilde{M} = 1^T (L + \beta y 1^T) \tilde{M} = \beta \sigma^m 1^T.
\]  

(2.4.25)

In the derivation of the diffusive mass fluxes we chose the regularization constant as \( \alpha = 1/ (\rho \text{max}(D_{ij})) \), by arguing that the regularization matrix should be of the same order of magnitude as the modified friction matrix \( \tilde{H} \). Although, this seems appropriate, we can also investigate the effect of different regularization constants on the diffusion matrix. This is done by computing the condition number of the diffusion matrix using

\[
\text{cond}(A) = \|A\|_\infty \|A^{-1}\|_\infty,
\]  

(2.4.26)

where \( \|\cdot\|_\infty \) denotes the \( \infty \)-norm over the matrix. A matrix with a low condition number is well-conditioned, while a matrix with a high condition number is ill-conditioned. An ill-conditioned matrix is also said to be sensitive to perturbations. Typically, if the condition number is \( \text{cond}(A) = \).
10^k$, then up to $k$ digits of accuracy may be lost in solving the system $Ax = b$ [20]. Next, we will denote with

$$\alpha^* = \frac{1}{\rho \max(D_{ij})}, \quad (2.4.27)$$

the usual regularization constant and $E^*$ the diffusion matrix computed using this regularization constant.

Consider now a mixture of hydrogen, nitrogen, argon, oxygen and water at a uniform pressure of $p = 10^2$ Pa and temperature $T = 300$ K. The mass fractions of the species are listed in table 2.1. The effect of the regularization constant on the condition number of the diffusion matrix is shown in figure 2.1. Furthermore, the condition number using the usual regularization constant $\alpha^*$ is given by $\text{cond}(E^*) = 3.33 \cdot 10^2$. The figure shows that the condition number increases by several orders of magnitude if a regularization constant is chosen several orders of magnitude lower or higher than the usual $\alpha^*$. There is a minimum at a different $\alpha$ than $\alpha^*$, however, for this $\alpha$ the condition number is roughly $0.5 \text{cond}(E^*)$. Since, the order of magnitude of a condition number is important rather than the exact value, the chosen $\alpha^*$ still is appropriate. Additionally, the optimal regularization constant depends on the mixture composition and conditions, therefore it changes when the mass fractions, pressure and temperature are changed. To conclude, the regularization constant given by equation (2.4.27) is indeed an appropriate choice.

Table 2.1: The mass fractions $y$ for a mixture.

<table>
<thead>
<tr>
<th>$y_i$</th>
<th>$y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.02</td>
</tr>
<tr>
<td>Ar</td>
<td>0.2</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.12</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure 2.1: The condition number of the diffusion matrix $\text{cond}(E)$ as a function of the regularization constant $\alpha$. Using the usual regularization constant $\alpha^*$, the condition number is $\text{cond}(E^*) = 3.33 \cdot 10^2$. Parameters: $p = 10^2$ Pa and $T = 300$ K.

2.4.3 Ambipolar diffusion

In a quasi-neutral plasma the current density $\vec{j}$ should be divergence-free, according to charge conservation [2.2.12], since $\sigma^e = 0$. The electric field required to maintain this quasi-neutrality is called
the ambipolar electric field $\vec{E}_{\text{amb}}$. The electric field causes forced diffusion. In addition to ordinary diffusion, the driving forces become

$$d^k = \frac{\partial}{\partial x^k} \mathbf{X} - \rho_c \frac{E^k_{\text{amb}}}{p}, \quad \forall k \in \{1, 2, 3\},$$

(2.4.28)

where $\rho_c = (n_1 q_1, \ldots, n_m q_m)^T$ is the vector of charge densities. The diffusive mass fluxes are now given by

$$J^k = -L \left( \frac{\partial}{\partial x^k} \mathbf{X} - \rho_c \frac{E^k_{\text{amb}}}{p} \right).$$

(2.4.29)

Since the current density should be divergence-free, there is an additional constraint on the system. The diffusive mass fluxes should now satisfy the constraint

$$j^k = \rho_c^T v^k = 0,$$

(2.4.30)

where we have assumed the zero-current constraint. This constraint can alternatively be written as

$$r^T J^k = 0,$$

(2.4.31)

where $r = (q_1/m_1, \ldots, q_m/m_m)^T$ is vector describing the ratio between charge and mass for each species $S_i$. Next, premultiplying the diffusive mass fluxes (2.4.29) with $r^T$ results in

$$\frac{E^k_{\text{amb}}}{p} = \frac{r^T L}{r^T L \rho_c} \frac{\partial}{\partial x^k} \mathbf{X}.$$

(2.4.32)

Substituting this again in expression (2.4.29) gives

$$J^k = -L \left( I - \rho_c r^T L \right) \frac{\partial}{\partial x^k} \mathbf{X} = -\hat{L} \frac{\partial}{\partial x^k} \mathbf{X},$$

(2.4.33)

where

$$\hat{L} = L \left( I - \rho_c r^T L \right).$$

(2.4.34)

The diffusive mass fluxes in terms of mass fraction gradients can again be obtained by using the conversion matrix $\tilde{M}$ given by (2.4.22), resulting in

$$J^k = -\mathcal{E} \frac{\partial}{\partial x^k} y,$$

(2.4.35)

where $\mathcal{E}$ is the ambipolar diffusion matrix given by

$$\mathcal{E} = \hat{L} \tilde{M}.$$

(2.4.36)

The ambipolar diffusion matrix still contains the mass and charge singularities, i.e, $1^T$ and $r^T$ are in the left nullspace. Therefore, we regularize the diffusion matrix using [10, eq. (32)]

$$\tilde{\mathcal{E}} = \hat{L} \tilde{M} + \beta y 1^T + \gamma \rho_c r^T,$$

(2.4.37)

with $\beta = \alpha^{-1} (\sigma^m)^{-2} = (\sigma^m)^{-2} \rho \max(D_{ij})$, according to (2.4.16), and $\gamma$ is defined by

$$\gamma := \max \left( \frac{\mathcal{E}}{\rho_c^T r} \right),$$

(2.4.38)

where $\max(\mathcal{E}) = \max(\mathcal{E}_{ij})$ denotes the maximum over the elements of the matrix.
Mass conservation in the ambipolar diffusion matrix is obtained by premultiplying with $1^T$, resulting in

$$1^T \mathcal{E} = 1^T \tilde{L} \tilde{M} + \beta 1^T y 1^T + \gamma 1^T \rho_e r^T$$

$$= \beta \sigma m 1^T + \gamma \rho \sigma r^T$$

$$= \beta \sigma m 1^T,$$  \hspace{1cm} (2.4.39)

where we have applied $\sigma^e = 0$ in the last step. Charge conservation for the ambipolar diffusion matrix can be found if $r^T$ is a left eigenvector. Indeed, we find

$$r^T \mathcal{E} = r^T \tilde{L} \tilde{M} + \beta r^T y 1^T + \gamma r^T \rho_e r^T$$

$$= \beta \sigma^t 1^T + \gamma r^T \rho_e r^T$$

$$= \gamma r^T \rho_e r^T,$$  \hspace{1cm} (2.4.40)

where we have applied $\sigma^e = 0$ in the last step.

### 2.5 Summary

In this chapter the conservation laws and reaction source terms of a multicomponent mixture have been discussed. Furthermore, the momentum equations for each species have been replaced by a simplified momentum balance given by the Stefan-Maxwell equations. The mass conservation laws (2.2.7) can therefore be described by a mass-averaged velocity for the mixture and a diffusive velocity for each species. The diffusive velocities can be obtained from the set of Stefan-Maxwell equations. The mass conservation laws for a mixture can be collected in vector-format as

$$\frac{\partial \rho y}{\partial t} + \sum_{k=1}^{3} \frac{\partial}{\partial x^k} \left( \rho u^k y - \mathcal{E}^k \frac{\partial y}{\partial x^k} \right) = \text{diag}(m) \omega.$$  \hspace{1cm} (2.5.1)

Here, the diffusion matrix $\mathcal{E}^k$ per coordinate is given by equation (2.4.24) when only considering ordinary diffusion or by (2.4.37) when considering ordinary diffusion and ambipolar diffusion. Furthermore, the reaction source term $\omega$ is given by equation (2.3.5). These two terms describe the coupling between the different species mass fractions. Since, each reaction rate is linear with the densities of the involved reacting species, we can split the reaction vector in a general linear part of the reaction system and a general source term, i.e.,

$$\omega = C y + \omega_R,$$  \hspace{1cm} (2.5.2)

where $C$ is a reaction matrix and $\omega_R$ is the remaining part of the reaction vector. Taking into account this linear reaction matrix $C$ when solving this system numerically will be the topic of this thesis.
Chapter 3

FVM applied to diffusion-reaction equations

In this chapter the focus is on deriving flux approximation schemes for conservation laws where advection is absent. In the case were advection is important, there are already several complete flux schemes derived for conservation laws of advection-diffusion type, both scalar \[1, 2, 3, 4, 5, 6\] and vectorial \[1, 6\]. The flux approximations of those schemes are derived from a local advection-diffusion BVP, without considering a linearized source term. Similarly, the flux approximations derived in sections 3.1, 3.2 are computed from a local BVP. However, instead of solving an advection-diffusion type conservation law, the diffusion-reaction type is solved for where a linearized reaction term is taken into account. Both scalar and vectorial type conservation laws are considered. Deriving the flux approximations for the more involved generic conservation laws of advection-diffusion-reaction type will be the topic of chapter 4.

Similar to the complete flux schemes derived in the previously mentioned literature, the numerical flux approximations for these schemes will consist of a homogeneous flux and an inhomogeneous flux. If only the homogeneous flux is considered, then the scheme is referred to as the diffusion-reaction homogeneous flux (DR-HF) scheme. If both the homogeneous and inhomogeneous fluxes are considered, then the scheme is referred to as the diffusion-reaction complete flux (DR-CF) scheme.

First, the scalar diffusion-reaction complete flux scheme is derived in section 3.1. Next, the system diffusion-reaction complete-flux scheme is derived in section 3.2, where the coupling of the individual equations is taken into account. Then, the performances of the scalar scheme and system scheme are tested for several test problems in sections 3.3 and 3.4 respectively.

3.1 Scalar diffusion-reaction scheme

In this section the finite volume method (FVM) is applied to the following one-dimensional scalar diffusion-reaction problem

\[
\frac{d}{dx} \left(-\varepsilon \frac{d\varphi}{dx}\right) = c\varphi + s(\varphi),
\]  

(3.1.1)

where \(\varepsilon\) is the diffusion coefficient and \(c\varphi + s(\varphi)\) denotes the complete source term, with \(c\varphi\) the linear part of the source term. The flux is defined as

\[
f := -\varepsilon \frac{d\varphi}{dx},
\]  

(3.1.2)

therefore ODE (3.1.1) can be written as

\[
\frac{df}{dx} = c\varphi + s(\varphi).
\]  

(3.1.3)
Then, integrating equation \((3.1.3)\) over an interval \(I_j := \left[ x_{j-1/2}, x_{j+1/2} \right] \) we obtain

\[
f(x_{j+1/2}) - f(x_{j-1/2}) = \int_{x_{j-1/2}}^{x_{j+1/2}} (c\phi + s(\phi)) \, dx. \tag{3.1.4}\]

The numerical approximation of the flux \(f(x_{j+1/2})\) will be denoted by \(F_{j+1/2}\) and the integral is approximated using the midpoint rule, resulting in

\[
F_{j+1/2} - F_{j-1/2} = \Delta x \left( c_j\phi_j + s_j \right), \tag{3.1.5}\]

where \(c_j := c(x_j), \phi_j := \phi(x_j)\) and \(s_j := s(\phi_j)\). The numerical flux \(F_{j+1/2}\) is determined from the local boundary value problem (BVP) with constant diffusion coefficient \(\varepsilon\) and reaction coefficient \(c\), i.e.,

\[
-\varepsilon \frac{d^2 \phi}{dx^2} - c\phi = s(\phi), \quad x_j < x < x_{j+1}, \tag{3.1.7a}\]

\[
\phi(x_j) = \phi_j, \quad \phi(x_{j+1}) = \phi_{j+1}. \tag{3.1.7b}\]

The characteristic equation is given by

\[
\mu^2 + \frac{c}{\varepsilon} = 0, \tag{3.1.8}\]

where the sign of \(c\) determines whether the characteristic root \(\mu\) will be imaginary or real, since the diffusion coefficient is always positive \((\varepsilon > 0)\). Three different cases have to be considered

\[
c < 0 : \quad \omega^2 = -\frac{c}{\varepsilon}, \quad \mu = \pm \omega, \tag{3.1.9a}\]

\[
c > 0 : \quad \omega^2 = \frac{c}{\varepsilon}, \quad \mu = \pm i\omega, \tag{3.1.9b}\]

\[
c = 0 : \quad \mu = 0, \tag{3.1.9c}\]

where \(\omega > 0\). For \(\mu = 0\) the solution is given by

\[
\phi(x) = ax + \beta. \tag{3.1.10}\]

From the boundary conditions we obtain

\[
\phi(x) = (\phi_{j+1} - \phi_j) \frac{x - x_j}{\Delta x} + \phi_j. \tag{3.1.11}\]

The first two cases can be combined by introducing

\[
\nu := \begin{cases} 
1 & \text{if } c < 0, \\
i & \text{if } c > 0. 
\end{cases} \tag{3.1.12}\]
Then, the characteristic root is written as \( \mu = \pm j \nu \omega \) and we obtain the general solution
\[
\varphi(x) = \alpha e^{j \nu \omega x} + \beta e^{-j \nu \omega x}. \quad (3.1.13)
\]

From the boundary conditions the coefficients \( \alpha \) and \( \beta \) can be determined
\[
\alpha e^{j \nu \omega x} + \beta e^{-j \nu \omega x} = \varphi_j, \quad (3.1.14a)
\]
\[
\alpha e^{j+1 \nu \omega x} + \beta e^{-j+1 \nu \omega x} = \varphi_{j+1}, \quad (3.1.14b)
\]
where from the first relation we obtain
\[
e^{-j \nu \omega x} \beta = \varphi_j - \alpha e^{j \nu \omega x}. \quad (3.1.15)
\]

Substituting (3.1.15) in (3.1.14b) results in
\[
\alpha e^{j+1 \nu \omega x} + e^{-j \nu \omega x} (\varphi_j - \alpha e^{j \nu \omega x}) = \varphi_{j+1},
\]
\[
\iff \alpha (e^{j \nu \omega x} - e^{-j \nu \omega x}) e^{j \nu \omega x} = \varphi_{j+1} - \varphi_j e^{-j \nu \omega x},
\]
\[
\iff \alpha = (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} e^{-j \nu \omega x} (\varphi_{j+1} - \varphi_j e^{-j \nu \omega x}). \quad (3.1.16)
\]

Substituting equations (3.1.15) and (3.1.16) in the homogeneous solution (3.1.13) results in
\[
\varphi(x) = \alpha e^{j \nu \omega x} + \beta e^{-j \nu \omega x}
\]
\[
= \alpha e^{j \nu \omega x} + e^{-j \nu \omega x} e^{j \nu \omega x} (\varphi_j - \alpha e^{j \nu \omega x})
\]
\[
= \alpha (e^{j \nu \omega x} - e^{-j \nu \omega x}) e^{j \nu \omega x} + \varphi_j e^{-(x-x_j) \nu \omega}
\]
\[
= (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} (\varphi_{j+1} - \varphi_j e^{-j \nu \omega}) (e^{(x-x_j) \nu \omega} - e^{-(x-x_j) \nu \omega}) + \varphi_j e^{-(x-x_j) \nu \omega}.
\]

Next, we rewrite the coefficients. The coefficient for \( \varphi_{j+1} \) does not require any rewriting and is given by
\[
(e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} (e^{(x-x_j) \nu \omega} - e^{-(x-x_j) \nu \omega}), \quad (3.1.17)
\]
while the coefficient for \( \varphi_j \) is simplified using
\[
-e^{j \nu \omega x} (e^{(x-x_j) \nu \omega} - e^{-(x-x_j) \nu \omega}) + e^{-(x-x_j) \nu \omega}
\]
\[
= (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} e^{-j \nu \omega x} (e^{(x-x_j) \nu \omega} - e^{-(x-x_j) \nu \omega}) + e^{-(x-x_j) \nu \omega}
\]
\[
= (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} e^{-(x-x_{j+1}) \nu \omega} + e^{-(x-x_j) \nu \omega}.
\]

Finally, the homogeneous solution \( \varphi(x) \) reads
\[
\varphi(x) = (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} \times [-(e^{(x-x_{j+1}) \nu \omega} - e^{-(x-x_{j+1}) \nu \omega}) \varphi_j + (e^{(x-x_j) \nu \omega} - e^{-(x-x_j) \nu \omega}) \varphi_{j+1}]. \quad (3.1.20)
\]

Now we introduce the scaled coordinate \( \sigma(x) = (x-x_j) / \Delta x \), therefore the solution can be rewritten as
\[
\varphi(x) = (e^{j \nu \omega x} - e^{-j \nu \omega x})^{-1} \times [-(e^{(\sigma(x)-1) \Delta x \nu \omega} - e^{-(\sigma(x)-1) \Delta x \nu \omega}) \varphi_j + (e^{\sigma(x) \Delta x \nu \omega} - e^{-\sigma(x) \Delta x \nu \omega}) \varphi_{j+1}], \quad (3.1.21)
\]
which can be rewritten using sinh$(x)$ to

$$\varphi(x) = \frac{\sinh(\sigma(x)\Delta x\nu\omega)\varphi_{j+1} + \sinh((1 - \sigma(x))\Delta x\nu\omega)\varphi_j}{\sinh(\Delta x\nu\omega)}.$$  \hfill (3.1.22)

From this solution, we can obtain the homogeneous flux $f_{j+1/2}^h$ by

$$f_{j+1/2}^h = f(x_{j+1/2}) = -\varepsilon \frac{d\varphi(x)}{dx}(x_{j+1/2})$$

$$= -\varepsilon \nu\omega \frac{\cosh((1/2)\Delta x\nu\omega)(\varphi_{j+1} - \cosh((1/2)\Delta x\nu\omega)\varphi_j)}{2\sinh((1/2)\Delta x\nu\omega)\cosh((1/2)\Delta x\nu\omega)} |_{x=x_{j+1/2}}$$

$$= -\varepsilon\nu\omega \frac{1}{2\Delta x\sinh((1/2)\Delta x\nu\omega)} (\varphi_{j+1} - \varphi_j)$$

$$= -\frac{\varepsilon}{\Delta x\sinh((1/2)\Delta x\nu\omega)} \varphi_{j+1} - \varphi_j.$$  \hfill (3.1.23)

Here, we have introduced the function sinh$\chi$ which is defined by

$$\text{sinhc}(z) := \frac{\sinh(z)}{z},$$  \hfill (3.1.24)

with sinh$\chi(0) = 1$. Next, we introduce the diffusive grid Damköhler number

$$D := \frac{|c|}{(\Delta x)^2} = \frac{(\omega\Delta x)^2}{\varepsilon},$$  \hfill (3.1.25)

describing the reaction rate over diffusive transport rate for the local BVP (3.1.7a)-(3.1.7b). Then, the homogeneous flux is given by

$$f_{j+1/2}^h = -\frac{\varepsilon}{\Delta x\sinh((1/2)\nu\sqrt{D})} \varphi_{j+1} - \varphi_j.$$  \hfill (3.1.26)

For the numerical flux we take $F_{j+1/2}^h = f_{j+1/2}^h$. The homogeneous flux $f_{j+1/2}^h$ is reminiscent of the central difference scheme, with a correction factor $1/\sinh((1/2)\nu\sqrt{D})$. In the limit where $c = 0$, the homogeneous flux (3.1.26) is still valid and actually reduces to the flux for the central difference, given by

$$f_{j+1/2}^h = -\frac{\varepsilon}{\Delta x} (\varphi_{j+1} - \varphi_j).$$  \hfill (3.1.27)

Considering the sign of the reaction coefficient $c$ the correction factor reduces to

$$\left(\sinhc\left(\frac{1}{2}\nu\sqrt{D}\right)\right)^{-1} = \begin{cases} \left(\sinhc\left(\frac{1}{2}\nu\sqrt{D}\right)\right)^{-1}, & \text{if } c < 0, \\ \left(\text{sinc}\left(\frac{1}{2}\nu\sqrt{D}\right)\right)^{-1}, & \text{if } c > 0, \end{cases}$$  \hfill (3.1.28)

where sinc$\chi := \sin(z)/z$ with sinc$\chi(0) = 1$. The functions sinh$\chi(z)$ and sinc$\chi(z)$ are plotted in figure 3.1. Therefore, if reaction is dominant then for $c < 0$ the usual diffusive flux is reduced, while for $c > 0$ the flux is increased. This is due to the destruction and production of $\varphi$, respectively. Note that the sinc$\chi(z)$ function has zeros at $z = k\pi$ for $k \in \mathbb{Z}\setminus\{0\}$. Therefore, the grid Damköhler number is restricted by $\frac{1}{2}\nu\sqrt{D} < \pi$ for $c > 0$. This constraint puts a requirement on the grid spacing $\Delta x$ for given diffusion and reaction coefficients, and this constraint is investigated in section 3.1.4.
3.1.2 Inhomogeneous flux

For the inhomogeneous flux we will consider the following local BVP

\[ -\varepsilon \frac{d^2 \varphi}{dx^2} - c \varphi = s(\varphi), \quad x_j < x < x_{j+1}, \]
\[ \varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}. \]  

In the following derivation the solution to the homogeneous ODE is used, given by

\[ \varphi^h(x) = \varphi_1(x)\varphi_j + \varphi_2(x)\varphi_{j+1}, \]

where \( \varphi_1(x) \) and \( \varphi_2(x) \) are the so-called fundamental solutions and are given by, cf. (3.1.22),

\[ \varphi_1(x) = \frac{\sinh \left( (1 - \sigma(x))\sqrt{\nu D} \right)}{\sinh(\nu \sqrt{D})}, \]
\[ \varphi_2(x) = \frac{\sinh \left( \sigma(x)\nu \sqrt{D} \right)}{\sinh(\nu \sqrt{D})}. \]

The fundamental solutions are solutions to the homogeneous BVP with boundary conditions \( \varphi_j = 1, \varphi_{j+1} = 0 \) and \( \varphi_j = 0, \varphi_{j+1} = 1 \) for \( \varphi_1(x) \) and \( \varphi_2(x) \), respectively. Next, we will apply variation of constants in order to determine the inhomogeneous solution \( \varphi^i(x) \). I.e.,

\[ \varphi^i(x) = a_1(x)\varphi_1(x) + a_2(x)\varphi_2(x), \]

and assume that

\[ a_1'(x)\varphi_1(x) + a_2'(x)\varphi_2(x) = 0, \]

where the prime \( ' \) denotes \( \frac{d}{dx} \). This condition is used such that the system for \( a_1(x) \) and \( a_2(x) \) can be solved. Then, substituting \( \varphi^i(x) \) in (3.1.29a) and using the fact that \( \varphi_1(x) \) and \( \varphi_2(x) \) are solutions of the homogeneous ODE, we obtain

\[ -\varepsilon \left( a_1'(x)\varphi_1(x) + a_2'(x)\varphi_2(x) \right) = s(\varphi(x)). \]
The functions \(a_1(x)\) and \(a_2(x)\) can then be found by solving the system \([3.1.33]-[3.1.34]\), resulting in

\[
\begin{align*}
a_1(x) &= \int \frac{\varphi_2(x)s(\varphi(x))}{\varepsilon W(\varphi_1, \varphi_2)(x)} \, dx, \\
a_2(x) &= -\int \frac{\varphi_1(x)s(\varphi(x))}{\varepsilon W(\varphi_1, \varphi_2)(x)} \, dx,
\end{align*}
\tag{3.1.35a-b}
\]

where \(W(\varphi_1, \varphi_2)\) is the Wronskian of \(\varphi_1\) and \(\varphi_2\), given by

\[
W(\varphi_1, \varphi_2) = \begin{vmatrix} \varphi_1 & \varphi_2 \\ \varphi_1' & \varphi_2' \end{vmatrix} = \frac{\nu \sqrt{D}}{\Delta x} \frac{1}{\sinh(\nu \sqrt{D})}.
\tag{3.1.36}
\]

Substituting the expressions \([3.1.35a]-[3.1.35b]\) in \([3.1.32]\) and applying the boundary conditions \([3.1.29b]\), we obtain

\[
\varphi^i(x) = \varphi_1(x) \int_{x_j}^{x} \frac{\varphi_2(z)s(\varphi(z))}{\varepsilon W(\varphi_1, \varphi_2)(z)} \, dz + \varphi_2(x) \int_{x}^{x_{j+1}} \frac{\varphi_1(z)s(\varphi(z))}{\varepsilon W(\varphi_1, \varphi_2)(z)} \, dz.
\tag{3.1.37}
\]

Therefore, the inhomogeneous flux is given by

\[
f_{j+1/2}^i = -\varepsilon \frac{d\varphi^i(x)}{dx} (x_{j+1/2}) = \left[ f_1(x) \int_{x_j}^{x} \frac{\varphi_2(z)s(\varphi(z))}{\varepsilon W(\varphi_1, \varphi_2)(z)} \, dz + f_2(x) \int_{x}^{x_{j+1}} \frac{\varphi_1(z)s(\varphi(z))}{\varepsilon W(\varphi_1, \varphi_2)(z)} \, dz \right]_{x=x_{j+1/2}}
\]

\[
= \frac{1}{\varepsilon} f_{1,j+1/2} \int_{x_j}^{x_{j+1/2}} \frac{\varphi_2(z)s(\varphi(z))}{W(\varphi_1, \varphi_2)(z)} \, dz + \frac{1}{\varepsilon} f_{2,j+1/2} \int_{x_{j+1/2}}^{x_{j+1}} \frac{\varphi_1(z)s(\varphi(z))}{\varepsilon W(\varphi_1, \varphi_2)(z)} \, dz,
\tag{3.1.38}
\]

where \(f_{1,j+1/2}^h\) and \(f_{2,j+1/2}^h\) correspond to the flux values at the interface \(x = x_{j+1/2}\) for the fundamental solutions \(\varphi_1(x)\) and \(\varphi_2(x)\), see \([3.1.26]\). The inhomogeneous flux can be written as

\[
f_{j+1/2}^i = \Delta x \int_0^1 G(\sigma; D)s(\varphi(x(\sigma))) \, d\sigma,
\tag{3.1.39}
\]

with \(G(\sigma; D)\) the Green’s function relating the flux to the source term and is given by

\[
G(\sigma; D) = \frac{1}{2 \sinh(\frac{1}{2} \nu \sqrt{D})} \begin{cases} 
\sinh(\sigma \nu \sqrt{D}), & \text{for } 0 \leq \sigma \leq \frac{1}{2}, \\
-\sinh(1 - \sigma) \nu \sqrt{D}, & \text{for } \frac{1}{2} < \sigma \leq 1.
\end{cases}
\tag{3.1.40}
\]

The Green’s function satisfies \(G(1^-; D) - G(1^+; D) = 1\), i.e., the Green’s function is discontinuous at \(\sigma = \frac{1}{2}\) with jump 1, see figure 3.2.

The numerical inhomogeneous flux \(F_{j+1/2}^i\) can be derived by assuming that the source is constant in the interval \(x_j < x < x_{j+1}\), i.e., \(s(\varphi) = s_j\). The integrals for the inhomogeneous flux can then be found to be

\[
\int_0^{\frac{1}{2}} \sinh(\sigma \nu \sqrt{D}) \, d\sigma = \frac{1}{\nu \sqrt{D}} \left( \cosh \left( \frac{1}{2} \nu \sqrt{D} \right) - 1 \right),
\]

\[
\int_{\frac{1}{2}}^1 \sinh \left( (1 - \sigma) \nu \sqrt{D} \right) \, d\sigma = \frac{1}{\nu \sqrt{D}} \left( \cosh \left( \frac{1}{2} \nu \sqrt{D} \right) - 1 \right),
\]

therefore both contributions cancel each other and the resulting numerical inhomogeneous flux is given by \(F_{j+1/2}^i = 0\).
3.1. Scalar diffusion-reaction scheme

If instead the source is assumed to be constant on the control volume \( x_{j-1/2} < x < x_{j+1/2} \), i.e.,

\[
s(\varphi) = \begin{cases} 
  s_j, & \text{for } x_{j-1/2} < x < x_{j+1/2}, \\
  s_{j+1}, & \text{for } x_{j+1/2} < x < x_{j+3/2},
\end{cases}
\]  

then the numerical inhomogeneous flux is found to be

\[
F_{j+1/2}^i = -\frac{\Delta x}{2\nu\sqrt{D}\sinh\left(\frac{1}{2}\nu\sqrt{D}\right)} \left( \cosh\left(\frac{1}{2}\nu\sqrt{D}\right) - 1 \right) (s_j - s_{j+1}).
\]

which can be rewritten to

\[
F_{j+1/2}^i = \Delta x \frac{s_j - s_{j+1}}{8} \tanh\left(\frac{1}{4}\nu\sqrt{D}\right).
\]

Here, we have introduced the function \( \tanhc(z) \) which is defined by

\[
\tanhc(z) := \frac{\tanh(z)}{z},
\]

with \( \tanhc(0) = 1 \). Considering the sign of the reaction coefficient \( c \) the factor reduces to

\[
\tanh\left(\frac{1}{4}\nu\sqrt{D}\right) = \begin{cases} 
  \tanh\left(\frac{1}{4}\sqrt{D}\right), & \text{if } c < 0, \\
  \tanc\left(\frac{1}{4}\sqrt{D}\right), & \text{if } c > 0,
\end{cases}
\]

where \( \tanc(z) := \tan(z)/z \) with \( \tanc(0) = 1 \). The functions \( \tanhc(z) \) and \( \tanc(z) \) are plotted in figure 3.3. Therefore, if reaction is dominant then for \( c < 0 \) the inhomogeneous flux is reduced, representing the fact that the source term \( s(\varphi) \) is not being transported and thus local source balances \((c\varphi + s(\varphi))\) determine the value of \( \varphi \). While, if reaction is dominant then for \( c > 0 \) the inhomogeneous flux is increased, similar to the homogeneous flux. Furthermore, the \( \tanc(z) \) function goes to \( \pm\infty \) at \( z = (k + \frac{1}{2})\pi \) for \( k \in \mathbb{Z}\setminus\{0\} \). The grid Damköhler number is restricted by \( \frac{1}{2}\sqrt{D} < \pi \) for \( c > 0 \), similar to restriction required for the homogeneous flux.

3.1.3 Scheme overview

Now, that the homogeneous and inhomogeneous fluxes have been computed, we can summarise the resulting schemes. To recap, the flux balance for the diffusion-reaction type conservation law is given
Chapter 3. FVM applied to diffusion-reaction equations

by (3.1.5), and reads

$$F_{j+1/2} - F_{j-1/2} = \Delta x \left(c_j \phi_j + s_j\right).$$

(3.1.46)

For the diffusion-reaction homogeneous flux (DR-HF) scheme, we only use the homogeneous flux given by (3.1.26), i.e.,

$$F_{j+1/2} = F^h_{j+1/2} = F^h_{j+1/2} = -\frac{\varepsilon}{\Delta x} \frac{\phi_{j+1} - \phi_j}{\sinh \left(\frac{1}{2} \sqrt{D}\right)}.$$

(3.1.47a)

If additionally the inhomogeneous flux (3.1.43) is taken into account, then the scheme is referred to as the diffusion-reaction complete flux (DR-CF) scheme, i.e.,

$$F_{j+1/2} = F^h_{j+1/2} + F^i_{j+1/2},$$

(3.1.48a)

$$F^h_{j+1/2} = -\frac{\varepsilon}{\Delta x} \frac{\phi_{j+1} - \phi_j}{\sinh \left(\frac{1}{2} \sqrt{D}\right)},$$

(3.1.48b)

$$F^i_{j+1/2} = \Delta x \left(s_j - s_{j+1}\right) + \frac{1}{8} \tanhc \left(\frac{1}{4} \sqrt{D}\right).$$

(3.1.48c)

These schemes can be compared with the classical standard central difference (CD) scheme, where the numerical flux is given by (3.1.27), i.e.,

$$F_{j+1/2} = F^h_{j+1/2},$$

(3.1.49a)

$$F^h_{j+1/2} = -\frac{\varepsilon}{\Delta x} \left(\phi_{j+1} - \phi_j\right).$$

(3.1.49b)

Note, that we do not take any inhomogeneous flux into account in the CD scheme.

3.1.4 Grid restrictions

In the derivations of the homogeneous flux, see section 3.1.1 and inhomogeneous flux, see section 3.1.2, there are restrictions put on the grid spacing $h := \Delta x$ when $c > 0$. I.e., the condition $\frac{1}{2} \sqrt{D} < \pi$, with $D > 0$, puts a requirement on the minimum number of gridpoints that must be used. This requirement will be further elaborated in this section.
Consider the following homogeneous BVP

\[ \varepsilon \frac{d^2 \varphi}{d \tilde{x}^2} + c \varphi = 0, \quad 0 < \tilde{x} < a, \]  

with \( c > 0 \). The BVP is made dimensionless with \( \tilde{x} = ax \), reducing the BVP to

\[ \frac{d^2 \varphi}{d x^2} + D \left( \frac{a}{h} \right)^2 \varphi(x) = 0, \quad 0 < x < 1. \]

The fraction \( n - 1 := \frac{a}{h} \) describes the number of gridpoints used. Next, we choose \( \sqrt{D} = 2\pi \), such that the oscillation frequency is given by

\[ \omega = 2\pi(n - 1). \]

Then, the exact solution reads

\[ \varphi(x) = \alpha \cos (\omega x) + \beta \sin (\omega x). \]

Applying the boundary conditions \( \varphi(0) = 0 \) and \( \varphi'(1) = \omega \), results in

\[ \varphi(x) = \sin (\omega x). \]

Let now \( n = 9 \), then the solution is given in figure 3.4. The blue line represents the exact solution, while the black dots represent the values on the numerical grid. If \( \frac{1}{2} \sqrt{D} = \pi \) then due to aliasing the numerical solution cannot be represented correctly, since then for every period there is exactly 1 gridpoint. If we would choose even fewer gridpoints, then there are fewer gridpoints than oscillations.

The grid restriction \( \frac{1}{2} \sqrt{D} < \pi \), therefore, is natural in order to resolve the oscillations of a solution.

### 3.1.5 Local discretisation error

Generally, in a discretised system the vector of unknowns \( u \) will be solved from

\[ Au = f, \]

where \( A \) is the discretisation matrix with coefficients as appearing in the discretised system and \( f \) contains the forcing and boundary data. The dimensions of \( A, u \) and \( f \) need to be the same as the original problem, i.e., no scaling with a grid spacing \( h \). The local discretisation error is defined

\[ Au^* =: f + d, \]
where \( u^* \) is the exact solution restricted to the grid. The *global discretisation error* is defined by

\[
e := u^* - u. \tag{3.1.57}
\]

Combining this with equations (3.1.55) and (3.1.56), and using that the matrix \( A \) is constant results in

\[
A e = d. \tag{3.1.58}
\]

The definition of the local discretisation error will now be applied to the HF scheme obtained from equations (3.1.5) and (3.1.26) with \( s_j = 0 \), i.e., the discretisation of \( \varepsilon \varphi'' + c \varphi = 0 \). The discretised scheme is then given by

\[
-\frac{\varepsilon}{(\Delta x)^2} \frac{\varphi_{j-1} - 2 \varphi_j + \varphi_{j+1}}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)} = c \varphi_j. \tag{3.1.59}
\]

Let \( h := \Delta x \). The local discretisation error is found from

\[
d_j = -\frac{\varepsilon}{h^2} \frac{\varphi(x_{j-1}) - 2 \varphi(x_j) + \varphi(x_{j+1})}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)} - c \varphi(x_j),
\]

where \( \varphi(x_{j-1}) \) and \( \varphi(x_{j+1}) \) will be approximated using a Taylor expansion about \( \varphi(x_j) \), and \( \varphi(x_j) \) denotes the exact solution of \( \varphi_j \). From the Taylor expansions only the even terms will remain, thus the local discretisation error is given by

\[
d_j = -\frac{\varepsilon}{h^2} \frac{2 \varphi(x_j) + h^2 \varphi''(x_j) + \frac{h^4}{12} \varphi^{(4)}(x_j) - 2 \varphi(x_j) + O(h^6)}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)} - c \varphi(x_j)
\]

\[
= -\frac{\varepsilon}{h^2} \frac{h^2 \varphi''(x_j) + \frac{h^4}{12} \varphi^{(4)}(x_j)}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)} - c \varphi(x_j)
\]

\[
= -\frac{\varepsilon}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)} \frac{h^2 \varphi'(x_j) + \frac{h^4}{12} \varphi^{(4)}(x_j) + O(h^4)}{1 - \frac{1}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)}} + O(h^4), \tag{3.1.60}
\]

where in the second step \( c \varphi(x_j) = -\varepsilon \varphi''(x_j) \) was used.

The discretisation error will be investigated in the limit \( h \to 0 \), and subsequent limits for \( \omega \ll 1 \) and \( \omega \gg 1 \), where \( \omega := \sqrt{\|e\|} / \varepsilon = \sqrt{D}/h \). Also two different cases will be discussed, because for \( c < 0 \) we have \( \nu = 1 \) and for \( c > 0 \) we have \( \nu = i \). The discretisation error will be split in the following two terms:

\[
R_1 := -\frac{\varepsilon}{\sinh \left( \frac{1}{2} \nu \omega h \right)} \frac{\frac{h^2}{12} \varphi^{(4)}(x_j)}{12} - \frac{h^2}{12} \varphi^{(4)}(x_j), \tag{3.1.61a}
\]

\[
R_2 := \varepsilon \varphi''(x_j) \left( 1 - \frac{1}{\sinh \left( \frac{1}{2} \nu \omega h \right)} \right), \tag{3.1.61b}
\]

such that \( d_j = R_1 + R_2 + O(h^4) \). In order to investigate the limit \( h \to 0 \) we will Taylor expand both terms using

\[
\frac{1}{\sinh(z)} = 1 - \frac{z^2}{6} + \frac{7z^4}{360} + O(z^6), \tag{3.1.62}
\]
3.2. System diffusion-reaction scheme

which is also valid when \( \nu = i \), i.e.,

\[
\frac{1}{\sinhc(iz)} = \frac{1}{\text{sinc}(z)} = 1 + \frac{z^2}{6} + \frac{7z^4}{360} + O(z^6).
\]  

Therefore the terms \( R_1 \) and \( R_2 \) reduce to

\[
R_1 = -\frac{\epsilon}{12} h^2 \varphi^{(4)}(x_j) + O(h^4), \tag{3.1.64a}
\]

\[
R_2 = \frac{\epsilon \nu^2 \omega^2}{24} h^2 \varphi''(x_j) + O(h^4). \tag{3.1.64b}
\]

By differentiating the ODE twice, and using \( \omega^2 = -\nu^2 c/\epsilon \) and \( \nu^4 = 1 \), we obtain \( \varphi^{(4)} = -c/\epsilon \varphi'' = \omega^2 \nu^2 \varphi'' \), therefore

\[
R_1 = -\frac{\epsilon \nu^2 \omega^2}{12} h^2 \varphi''(x_j) + O(h^4). \tag{3.1.65}
\]

Thus the discretisation error is given by

\[
d_j = R_1 + R_2 + O(h^4) = -\frac{\epsilon \nu^2 \omega^2}{24} h^2 \varphi''(x_j) + O(h^4). \tag{3.1.66}
\]

First the discretisation error will be investigated when \( c < 0 \), i.e., \( \nu = 1 \), in the limits \( \omega \ll 1 \) and \( \omega \gg 1 \), with \( \epsilon \) fixed. Then from (3.1.66) it immediately follows that

\[
d_j = -\epsilon \omega^2 h^2 \varphi''(x_j)/24 + O(h^4), \tag{3.1.67}
\]

and since \( \omega \ll 1 \) is small, \( d_j \) is \( O(h^2) \) if \( \varphi(x) \) is sufficiently smooth. For \( \omega \gg 1 \) we still require \( \omega h \ll 1 \) due to the grid restriction, therefore the above relation still holds for \( \omega \gg 1 \).

For \( \nu = i \) \((c > 0)\) the discretisation error is given by \( d_j \approx \epsilon \omega^2 h^2 \varphi''(x_j)/24 \). For \( \nu = i \) we only need to investigate the limit \( \omega \ll 1 \), since the oscillations can only be presented well if \( \omega h < 1 \). Therefore, \( d_j \) is \( O(h^2) \) if \( \varphi(x) \) is sufficiently smooth.

The local discretisation error using the standard central difference scheme for this problem can be derived to be

\[
d_j = -\frac{\epsilon}{h^2} \left( 2\varphi(x_j) + h^2 \varphi''(x_j) + \frac{h^4}{12} \varphi^{(4)}(x_j) - 2\varphi(x_j) \right) - \epsilon \varphi(x_j) + O(h^4)
\]

\[
= -\frac{\epsilon}{h^2} \left( h^2 \varphi''(x_j) + \frac{h^4}{12} \varphi^{(4)}(x_j) \right) + \epsilon \varphi''(x_j) + O(h^4)
\]

\[
= -\frac{h^2}{12} \varphi^{(4)}(x_j) + O(h^4)
\]

\[
= -\epsilon \omega^2 \nu^2 h^2 \varphi''(x_j) + O(h^4). \tag{3.1.68}
\]

Thus the newly derived homogeneous flux approximation scheme is twice as accurate compared to the standard central difference scheme.

3.2 System diffusion-reaction scheme

In this section the finite volume method is applied to a system of one-dimensional conservation laws of diffusion-reaction type. The following system is considered

\[
\frac{d}{dx} \left( \mathcal{E} \frac{d\varphi}{dx} \right) + C \varphi + s(\varphi) = 0, \tag{3.2.1}
\]
where $\mathcal{E} = (\varepsilon_{ij})$ is the positive-definite diffusion matrix and $C\varphi + s(\varphi)$ represents the complete source, with $C\varphi$ the linear part of the source. The matrix $C$ is referred to as the reaction matrix. Both the diffusion and reaction matrices have size $m \times m$. The vector $\varphi$ contains the unknown variables of interest. The flux vector $f$ can be introduced such that

$$f := -\mathcal{E} \frac{d\varphi}{dx}, \quad (3.2.2a)$$
$$\frac{df}{dx} = C\varphi + s(\varphi). \quad (3.2.2b)$$

Then, integrating equation (3.2.2b) over an interval $I_j = [x_{j-1/2}, x_{j+1/2}]$ we obtain

$$f(x_{j+1/2}) - f(x_{j-1/2}) = \int_{x_{j-1/2}}^{x_{j+1/2}} (C\varphi + s(\varphi)) \, dx. \quad (3.2.3)$$

The numerical approximation of the flux $f(x_{j+1/2})$ will be denoted by $F_{j+1/2}$ and the integral is approximated using the midpoint rule, resulting in

$$F_{j+1/2} - F_{j-1/2} = \Delta x (C_j \varphi_j + s_j), \quad (3.2.4)$$

where $C_j := C(x_j)$, $\varphi_j := \varphi(x_j)$ and $s_j := s(\varphi_j)$. The numerical flux $F_{j+1/2}$ is determined from the local BVP with constant diffusion matrix $\mathcal{E}$ and reaction matrix $C$, i.e.,

$$-\mathcal{E} \frac{d^2\varphi}{dx^2} - C\varphi = s(\varphi), \quad x_j < x < x_{j+1}, \quad (3.2.5a)$$
$$\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}. \quad (3.2.5b)$$

The numerical flux vector will consist of a homogeneous flux and an inhomogeneous flux, i.e., $F_{j+1/2} = F^{h}_{j+1/2} + F^{i}_{j+1/2}$. First, we will derive the homogeneous flux $F^{h}_{j+1/2}$ in section 3.2.1, followed by the derivation of the inhomogeneous flux $F^{i}_{j+1/2}$ in section 3.2.2. The resulting schemes are summarised in section 3.2.3 and, finally, discrete mass and charge conservation for these schemes is investigated in section 3.2.4.

### 3.2.1 Homogeneous flux

The homogeneous flux vector is found by solving the local BVP

$$\mathcal{E} \frac{d^2\varphi}{dx^2} + C\varphi = 0, \quad x_j < x < x_{j+1}, \quad (3.2.6a)$$
$$\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}. \quad (3.2.6b)$$

Since $\mathcal{E}$ is regular, the system ODE (3.2.6a) can be rewritten using the matrix

$$A := \mathcal{E}^{-1}C, \quad (3.2.7)$$

resulting in

$$\frac{d^2\varphi}{dx^2} + A\varphi = 0. \quad (3.2.8)$$

It is assumed that the matrix $A$ has $m$ real eigenvalues $\lambda_k$, which can be negative, with corresponding eigenvectors $v_k$. Thus

$$\lambda_1 \leq \lambda_2 \leq \ldots \leq \lambda_n \leq 0 < \lambda_{n+1} \leq \ldots \leq \lambda_m. \quad (3.2.9)$$

Additionally, assume that the matrix $A$ has a complete set of eigenvectors:

$$A v_k = \lambda_k v_k \Leftrightarrow (C - \lambda_k \mathcal{E}) v_k = 0 \quad (k = 1, 2, \ldots, m). \quad (3.2.10)$$
3.2. System diffusion-reaction scheme

Then, the (spectral) decomposition of $A$ is given by

$$A = V \Lambda V^{-1}, \quad \Lambda := \text{diag} (\lambda_1, \lambda_2, ..., \lambda_m), \quad V := (v_1 v_2 ... v_m),$$  \hspace{1cm} (3.2.11)

with $A$ and $V$ constant matrices. Based on this decomposition any matrix function $g(A)$ can be determined by \cite{22}

$$g(A) = V g(\Lambda) V^{-1},$$ \hspace{1cm} (3.2.12a)

$$g(\Lambda) = \text{diag} (g(\lambda_1), g(\lambda_2), ..., g(\lambda_m)).$$ \hspace{1cm} (3.2.12b)

The computation of a product of two matrix functions with the same matrix is, therefore, given by

$$g(A) h(A) = V g(\Lambda) V^{-1} V h(\Lambda) V^{-1} = V h(\Lambda) V^{-1} V g(\Lambda) V^{-1} = h(A) g(A).$$ \hspace{1cm} (3.2.13)

I.e., the two matrix functions can be interchanged since the matrix function only modifies the eigenvalues but not the eigenvectors. Therefore, the matrix functions $g(A)$ and $h(A)$ commute.

Next, premultiplying the system ODE (3.2.8) with $V^{-1}$ results in

$$V^{-1} \frac{d^2 \varphi}{dx^2} + V^{-1} A \varphi = 0 \Leftrightarrow V^{-1} \frac{d^2 \varphi}{dx^2} + \Lambda V^{-1} \varphi = 0.$$ \hspace{1cm} (3.2.14)

Since $V$ is constant, $V^{-1}$ is also a constant matrix. Therefore, the vector $\psi$ is introduced, such that the system ODE can be written as

$$\psi := V^{-1} \varphi,$$ \hspace{1cm} (3.2.15a)

$$\frac{d^2 \psi}{dx^2} + \Lambda \psi = 0.$$ \hspace{1cm} (3.2.15b)

The system ODE is now decoupled and can be written componentwise as

$$\frac{d^2 \psi_k}{dx^2} + \lambda_k \psi_k = 0, \quad (k = 1, 2, ..., m).$$ \hspace{1cm} (3.2.16)

The characteristic equation $\mu^2 + \lambda_k = 0$ can be obtained for each component. Just as in the scalar variant, three different cases have to be considered

$$\lambda_k < 0 : \quad \lambda_k = -\omega_k^2, \quad \mu = \pm \omega_k,$$ \hspace{1cm} (3.2.17a)

$$\lambda_k > 0 : \quad \lambda_k = \omega_k^2, \quad \mu = \pm i \omega_k,$$ \hspace{1cm} (3.2.17b)

$$\lambda_k = 0 : \quad \mu = 0,$$ \hspace{1cm} (3.2.17c)

where $\omega_k > 0$. For $\lambda_k = 0$ the solution is given by

$$\psi_k(x) = \alpha_k x + \beta_k.$$ \hspace{1cm} (3.2.18)

The first two cases can be combined by introducing

$$\nu_k := \begin{cases} 1 & \text{if } \lambda_k < 0, \\ i & \text{if } \lambda_k > 0. \end{cases}$$ \hspace{1cm} (3.2.19)

Then, the characteristic root is written as $\mu = \pm \nu_k \omega_k$ and we obtain the general solution

$$\psi_k(x) = \alpha_k e^{\nu_k \omega_k x} + \beta_k e^{-\nu_k \omega_k x}.$$ \hspace{1cm} (3.2.20)
Collecting the components again in a vector, the general solution can be written as
\[ \psi(x) = \text{diag} \left( e^{\nu_k \omega_k x} \right) \alpha + \text{diag} \left( e^{-\nu_k \omega_k x} \right) \beta. \]
(3.2.21)

The vectors \( \alpha \) and \( \beta \) have to be determined from the boundary conditions \( \textbf{(3.2.6b)} \). Next, we define the auxiliary matrix \( \Omega \)
\[ \Omega := \text{diag} \left( \nu_k \omega_k \right), \]
(3.2.22)

for which the following relations hold
\[ e^{x \Omega} = \text{diag} \left( e^{x \nu_k \omega_k} \right), \]
\[ (e^{x \Omega})^{-1} = e^{-x \Omega} = \text{diag} \left( e^{-x \nu_k \omega_k} \right). \]
(3.2.23a)

Note that \( (\nu_k \omega_k)^2 = -\lambda_k \) and likewise for the matrix \( \Omega^2 = -\Lambda \). Then, the solution given by \( \textbf{(3.2.21)} \) can be written as
\[ \psi(x) = e^{x \Omega} \alpha + e^{-x \Omega} \beta. \]
(3.2.24)

Applying the boundary conditions from \( \textbf{(3.2.6b)} \) the vectors \( \alpha \) and \( \beta \) can be determined, i.e.,
\[ e^{x_j \Omega} \alpha + e^{-x_j \Omega} \beta = \psi_j =: V^{-1} \varphi_j, \]
(3.2.25a)
\[ e^{x_{j+1} \Omega} \alpha + e^{-x_{j+1} \Omega} \beta = \psi_{j+1} =: V^{-1} \varphi_{j+1}, \]
(3.2.25b)

where from the first relation we obtain
\[ e^{-x_j \Omega} \beta = \psi_j - e^{x_j \Omega} \alpha. \]
(3.2.26)

Note that \( e^{x_{j+1} \Omega} = e^{x_j \Omega} e^{\alpha x_j \Omega}, \) where \( x_j \Omega \) and \( \Delta x \Omega \) obviously commute. Then, substituting equation \( \textbf{(3.2.26)} \) in \( \textbf{(3.2.25b)} \) results in
\[ e^{\Delta x \Omega} e^{x_j \Omega} \alpha + e^{-\Delta x \Omega} \left( \psi_j - e^{x_j \Omega} \alpha \right) = \psi_{j+1}, \]
\[ \Leftrightarrow \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right) e^{x_j \Omega} \alpha = \psi_{j+1} - e^{-\Delta x \Omega} \psi_j, \]
\[ \Leftrightarrow \alpha = e^{-x_j \Omega} \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \left( \psi_{j+1} - e^{-\Delta x \Omega} \psi_j \right). \]
(3.2.27)

Substituting equations \( \textbf{(3.2.26)} \) and \( \textbf{(3.2.27)} \) in the general solution \( \textbf{(3.2.21)} \) results in
\[ \psi(x) = e^{x \Omega} \alpha + e^{-x \Omega} e^{x_j \Omega} \left( \psi_j - e^{x_j \Omega} \alpha \right) \]
\[ = \left( e^{x \Omega} - e^{-x \Omega} e^{2x_j \Omega} \right) \alpha + e^{-\left( x_j - x \right) \Omega} \psi_j \]
\[ = \left( e^{x \Omega} - e^{-x \Omega} e^{2x_j \Omega} \right) e^{x_j \Omega} \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \left( \psi_{j+1} - e^{-\Delta x \Omega} \psi_j \right) + e^{-\left( x_j - x \right) \Omega} \psi_j \]
\[ = \left( e^{x \Omega} - e^{-x \Omega} \right) e^{-\left( x_j - x \right) \Omega} \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \left( \psi_{j+1} - e^{-\Delta x \Omega} \psi_j \right) + e^{-\left( x_j - x \right) \Omega} \psi_j. \]
(3.2.28)

Next, we rewrite the coefficient matrices by repeatedly applying the commutation \( g(\Omega)h(\Omega) = h(\Omega)g(\Omega) \) given by relation \( \textbf{(3.2.13)} \). The coefficient matrix for \( \psi_{j+1} \) is written as
\[ \left( e^{x_j \Omega} - e^{-x_j \Omega} \right) \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} = \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \left( e^{x_j \Omega} - e^{-x_j \Omega} \right). \]
(3.2.29)

The coefficient matrix for \( \psi_j \) is simplified using
\[ \left( e^{x_{j+1} \Omega} + e^{-x_{j+1} \Omega} \right) \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} = \left( e^{x_{j+1} \Omega} \right) \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \]
\[ = \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \left( e^{x_{j+1} \Omega} \right). \]
(3.2.30)
Finally, the general solution for $\psi(x)$ reads

$$
\psi(x) = \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \times \left[ - \left( e^{(x-x_{j+1})\Omega} - e^{-(x-x_{j+1})\Omega} \right) \varphi_j + \left( e^{(x-x_j)\Omega} - e^{-(x-x_j)\Omega} \right) \varphi_{j+1} \right].
$$

(3.2.31)

The homogeneous solution $\varphi(x)$ is found by premultiplying (3.2.31) with $V$ and using the definition of $\psi$ given by (3.2.15a), i.e.,

$$
\varphi(x) = V \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \times \left[ - \left( e^{(x-x_{j+1})\Omega} - e^{-(x-x_{j+1})\Omega} \right) V^{-1} \psi_j + \left( e^{(x-x_j)\Omega} - e^{-(x-x_j)\Omega} \right) V^{-1} \psi_{j+1} \right] = V \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right)^{-1} \times \left[ - \left( e^{(x-x_{j+1})\Omega} - e^{-(x-x_{j+1})\Omega} \right) V^{-1} \varphi_j + \left( e^{(x-x_j)\Omega} - e^{-(x-x_j)\Omega} \right) V^{-1} \varphi_{j+1} \right].
$$

(3.2.32)

Next, we define the auxiliary matrix $B$ as

$$
B := V \Omega^{-1} V^{-1}.
$$

(3.2.33)

It can be easily verified that the following relations hold for $B$

$$
B^2 = -A, \quad e^{xB} = V e^{x\Omega} V^{-1}.
$$

(3.2.34)

Therefore, the homogeneous solution (3.2.32) can be written as

$$
\varphi(x) = \left( e^{\Delta x B} - e^{-\Delta x B} \right)^{-1} \times \left[ - \left( e^{(x-x_{j+1})B} - e^{-(x-x_{j+1})B} \right) \varphi_j + \left( e^{(x-x_j)B} - e^{-(x-x_j)B} \right) \varphi_{j+1} \right],
$$

(3.2.35)

where the following relation was used

$$
V \left( e^{x\Omega} - e^{-x\Omega} \right)^{-1} V^{-1} = \left( V \left( e^{\Delta x \Omega} - e^{-\Delta x \Omega} \right) V^{-1} \right)^{-1} = \left( e^{\Delta x B} - e^{-\Delta x B} \right)^{-1},
$$

and similarly for the second and third terms.

The following relations hold for the $\sinh(xB)$ and $\cosh(xB)$ matrix functions

$$
\sinh(xB) = \frac{1}{2} \left( e^{xB} - e^{-xB} \right), \quad \cosh(xB) = \frac{1}{2} \left( e^{xB} + e^{-xB} \right), \quad \frac{d\sinh(xB)}{dx} = B \cosh(xB),
$$

$$
\cosh(-xB) = \cosh(xB), \quad \sinh(2xB) = 2 \sinh(xB) \cosh(xB).
$$

(3.2.36)

Applying the first relation of (3.2.36) and introducing $\sigma(x) = (x-x_j)/\Delta x$, the homogeneous solution (3.2.35) can be written as

$$
\varphi(x) = \left( \sinh(\Delta x B) \right)^{-1} \left( \sinh((1-\sigma(x)) \Delta x B) \varphi_j + \sinh(\sigma(x) \Delta x B) \varphi_{j+1} \right).
$$

(3.2.37)

Applying the last three relations of (3.2.36) and using the definition of the flux (3.2.2a), we can obtain homogeneous flux $f^h_{j+1/2}$ by

$$
f^h_{j+1/2} = f(x_{j+1/2}) = -E \frac{d\varphi(x)}{dx}(x_{j+1/2})
$$

$$
= -E \left( \sinh(\Delta x B) \right)^{-1} B \left( - \cosh \left( \frac{1}{2} \Delta x B \right) \varphi_j + \cosh \left( \frac{1}{2} \Delta x B \right) \varphi_{j+1} \right)
$$

$$
= -E B \left( 2 \sinh \left( \frac{1}{2} \Delta x B \right) \cosh \left( \frac{1}{2} \Delta x B \right) \right)^{-1} \cosh \left( \frac{1}{2} \Delta x B \right) \left( \varphi_{j+1} - \varphi_j \right)
$$

$$
= -E B \frac{1}{2} \left( \sinh \left( \frac{1}{2} \Delta x B \right) \right)^{-1} \left( \varphi_{j+1} - \varphi_j \right).
$$

(3.2.38)
Next, we use the definition of the $\text{sinc}h(z)$ function from (3.1.24) and simplify using the following relation

$$
\frac{1}{\Delta x} \frac{1}{2} \Delta x B \left( \text{sinc}h \left( \frac{1}{2} \Delta x B \right) \right) = \frac{1}{\Delta x} \frac{1}{2} \Delta x V \Omega V^{-1} \left( \text{sinc}h \left( \frac{1}{2} \Delta x \Omega \right) \right) V^{-1}
$$

$$
= \frac{1}{\Delta x} V \left( \text{sinc}h \left( \frac{1}{2} \Delta x \Omega \right) \right) \left( \frac{1}{2} \Delta x \Omega \right)^{-1} V^{-1}
$$

$$
= \frac{1}{\Delta x} V \left( \text{sinc}h \left( \frac{1}{2} \Delta x \Omega \right) \right) V^{-1}
$$

$$
= \frac{1}{\Delta x} \left( \text{sinc}h \left( \frac{1}{2} \Delta x B \right) \right)^{-1}.
$$

Then, the homogeneous flux is given by

$$
f_{j+1/2}^{h} = -\frac{1}{\Delta x} E \left( \text{sinc}h \left( \frac{1}{2} \Delta x B \right) \right)^{-1} \left( \varphi_{j+1} - \varphi_{j} \right). \quad (3.2.39)
$$

Next, we introduce the diffusive grid Damköhler matrix by

$$
D := (\Delta x)^2 A = (\Delta x)^2 E^{-1} C. \quad (3.2.40)
$$

Also, we need the following auxiliary matrix $\hat{D}$

$$
\hat{D} := \Delta x B, \quad (3.2.41)
$$

which is related to the diffusive grid Damköhler matrix by $\hat{D}^2 = -D$. Now, the homogeneous flux can be written as

$$
f_{j+1/2}^{h} = -\frac{1}{\Delta x} E \left( \text{sinc}h \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \left( \varphi_{j+1} - \varphi_{j} \right). \quad (3.2.42)
$$

For the numerical flux we take $F_{j+1/2}^{h} = f_{j+1/2}^{h}$. The homogeneous flux for (3.2.42) is also valid in the case for singular $A$ matrix, i.e., when one or multiple eigenvalues have $\lambda_k = 0$. Furthermore, if the eigenvalues of $A$ are restricted by $\frac{1}{2} \sqrt{-\lambda_m} \Delta x < \pi$ in case $\lambda_m < 0$, then $\text{sinc}h(\hat{D})$ will be regular even when $\hat{D}$ is singular, as is the case for a singular reaction matrix.

In the limit that $C = 0$, then the homogeneous flux reduces to the system central difference (CD) homogeneous flux, given by

$$
F_{j+1/2}^{h} = -\frac{1}{\Delta x} E \left( \varphi_{j+1} - \varphi_{j} \right). \quad (3.2.43)
$$

### 3.2.2 Inhomogeneous flux

For the inhomogeneous flux vector we will consider the following local BVP

$$
-\mathcal{E} \frac{d^2 \varphi}{dx^2} - C \varphi = s(\varphi), \quad x_j < x < x_{j+1}, \quad (3.2.44a)
$$

$$
\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}. \quad (3.2.44b)
$$

First, we will decouple the ODE system (3.2.44a) by premultiplying by $V^{-1} \mathcal{E}^{-1}$, resulting in

$$
V^{-1} \frac{d^2 \varphi}{dx^2} + V^{-1} \mathcal{E}^{-1} C \varphi + V^{-1} \mathcal{E}^{-1} s(\varphi) = 0. \quad (3.2.45)
$$
Next, applying the relations (3.2.7) and (3.2.15a), and defining \( \mathbf{s} := \mathbf{V}^{-1} \mathbf{E}^{-1} \mathbf{s}(\varphi) \), we obtain
\[
\frac{d^2 \psi}{dx^2} + \Lambda \psi + \mathbf{s} = 0.
\] (3.2.46)

The ODE system is again decoupled and can be written componentwise as
\[
\frac{d^2 \psi_k}{dx^2} + \lambda_k \psi_k + \bar{s}_k = 0, \quad (k = 1, 2, ..., m). \tag{3.2.47}
\]

The boundary conditions for this system are defined in (3.2.25a)-(3.2.25b) and componentwise read
\[
\psi_k(x_j) = \psi_{k,j}, \quad \psi_k(x_{j+1}) = \psi_{k,j+1}, \quad (k = 1, 2, ..., m). \tag{3.2.48}
\]

Just like in the scalar case, we require the solution to the homogeneous ODE problem. The homogeneous solutions for \( \psi_k(x) \) can be found from (3.2.37), which are then given by
\[
\psi^h_k(x) = \psi_{k,1}(x) \psi_{k,j} + \psi_{k,2}(x) \psi_{k,j+1}, \tag{3.2.49}
\]

with \( \psi_{k,1}(x) \) and \( \psi_{k,2}(x) \) the fundamental solutions, given by
\[
\psi_{k,1}(x) = \frac{\sinh ((1 - \sigma(x)) \nu k \omega k \Delta x)}{\sinh (\nu k \omega k \Delta x)}, \tag{3.2.50a}
\]
\[
\psi_{k,2}(x) = \frac{\sinh (\sigma(x) \nu k \omega k \Delta x)}{\sinh (\nu k \omega k \Delta x)}. \tag{3.2.50b}
\]

Next, we will apply variation of constants in order to determine the inhomogeneous solution \( \psi^i_k(x) \). I.e.,
\[
\psi^i_k(x) = a_{k,1}(x) \psi_{k,1}(x) + a_{k,2}(x) \psi_{k,2}(x), \tag{3.2.51}
\]

and assume that
\[
a'_{k,1}(x) \psi_{k,1}(x) + a'_{k,2}(x) \psi_{k,2}(x) = 0, \tag{3.2.52}
\]

such that the system for \( a_{k,1}(x) \) and \( a_{k,2}(x) \) can be solved. Then, substituting \( \psi^i_k(x) \) in ODE (3.2.47) and use the fact that \( \psi_{k,1}(x) \) and \( \psi_{k,2}(x) \) are solutions of the homogeneous part of the ODE, we obtain
\[
- (a'_{k,1}(x) \psi_{k,1}(x) + a'_{k,2}(x) \psi_{k,2}(x)) = \bar{s}_k. \tag{3.2.53}
\]

The functions \( a_{k,1}(x) \) and \( a_{k,2}(x) \) can then be found by solving the system (3.2.52)-(3.2.53), resulting in
\[
a_{k,1}(x) = \int \frac{\psi_{k,2}(x) \bar{s}_k}{W(\psi_{k,1}, \psi_{k,2})(x)} \, dx, \tag{3.2.54a}
\]
\[
a_{k,2}(x) = - \int \frac{\psi_{k,1}(x) \bar{s}_k}{W(\psi_{k,1}, \psi_{k,2})(x)} \, dx, \tag{3.2.54b}
\]

where \( W(\psi_{k,1}, \psi_{k,2}) \) denotes the Wronskian. Note that \( \bar{s}_k \) depends on \( \varphi(x) \), and therefore also depends on \( \psi(x) \). The Wronskian is given by
\[
W(\psi_{k,1}, \psi_{k,2}) = \begin{vmatrix} \psi_{k,1} & \psi_{k,2} \\ \psi'_{k,1} & \psi'_{k,2} \end{vmatrix} = \frac{\nu k \omega k}{\sinh (\nu k \omega k \Delta x)}. \tag{3.2.55}
\]

Substituting the expressions (3.2.54a)-(3.2.54b) in (3.2.51) and applying the the boundary conditions (3.2.48), we obtain
\[
\psi^i_k(x) = \psi_{k,1}(x) \int_{x_j}^{x} \frac{\psi_{k,2}(z) \bar{s}_k}{W(\psi_{k,1}, \psi_{k,2})(z)} \, dz + \psi_{k,2}(x) \int_{x}^{x_{j+1}} \frac{\psi_{k,1}(z) \bar{s}_k}{W(\psi_{k,1}, \psi_{k,2})(z)} \, dz. \tag{3.2.56}
\]
Substituting (3.2.50a) and (3.2.50b) and (3.2.55) in (3.2.56), results in
\[
\psi_k^i(x) = \frac{\sinh \left( (1 - \sigma(x)) \nu_k \Delta x \right)}{\nu_k \sinh (\nu_k \Delta x)} \int_{x_j}^{x} \text{d}x \sinh (\sigma(z) \nu_k \Delta x) \tilde{s}_k (\psi(z)) \text{d}z
\]
\[+ \frac{\sinh (\sigma(x) \nu_k \Delta x)}{\nu_k \sinh (\nu_k \Delta x)} \int_{x}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \nu_k \Delta x \right) \tilde{s}_k (\psi(z)) \text{d}z. \tag{3.2.57}
\]

Alternatively, we can collect the components \(\psi_k^i(x)\) in a vector and using relation (3.2.33), resulting in
\[
\psi^i(x) = (\Omega \sinh (\Delta x \Omega))^{-1} \left[ \sinh \left( (1 - \sigma(x)) \Delta x \Omega \right) \int_{x_j}^{x} \text{d}x \sinh (\sigma(z) \Delta x \Omega) \tilde{s} (\psi(z)) \text{d}z \right.
\]
\[+ \sinh (\sigma(x) \Delta x \Omega) \int_{x}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \Delta x \Omega \right) \tilde{s} (\psi(z)) \text{d}z \right]. \tag{3.2.58}
\]

Next, the inhomogeneous solution \(\varphi^i(x)\) is found by premultiplying (3.2.58) with \(V\) using the definitions of \(\hat{D}\) and given by (3.2.41) and (3.2.15a), respectively. The result reads
\[
\varphi^i(x) = \Delta x \left( \hat{D} \sinh (\hat{D}) \right)^{-1} \left[ \sinh \left( (1 - \sigma(x)) \hat{D} \right) \int_{x_j}^{x} \text{d}x \sinh (\sigma(z) \hat{D}) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right.
\]
\[+ \sinh (\sigma(x) \hat{D}) \int_{x}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \hat{D} \right) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right]. \tag{3.2.59}
\]

Therefore, the inhomogeneous flux is given by
\[
f^i_{j+1/2} = -\mathcal{E} \frac{\text{d}\varphi^i(x)}{\text{d}x}(x_{j+1/2})
\]
\[= -\mathcal{E} \left( \sinh (\hat{D}) \right)^{-1} \left[ -\cosh \left( (1 - \sigma(x)) \hat{D} \right) \int_{x_j}^{x} \text{d}x \sinh (\sigma(z) \hat{D}) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right.
\]
\[+ \cosh (\sigma(x) \hat{D}) \int_{x}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \hat{D} \right) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right]_{x=x_{j+1/2}}
\]
\[= \mathcal{E} \left( 2 \sinh \left( \frac{1}{2} \hat{D} \right) \cosh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \left[ \cosh \left( \frac{1}{2} \hat{D} \right) \int_{x_j}^{x_{j+1/2}} \text{d}x \sinh (\sigma(z) \hat{D}) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right.
\]
\[\left. - \cosh \left( \frac{1}{2} \hat{D} \right) \int_{x_{j+1/2}}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \hat{D} \right) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right]
\]
\[= \mathcal{E} \left( 2 \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \left[ \int_{x_j}^{x_{j+1/2}} \text{d}x \sinh (\sigma(z) \hat{D}) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right.
\]
\[\left. - \int_{x_{j+1/2}}^{x_{j+1}} \text{d}x \sinh \left( (1 - \sigma(z)) \hat{D} \right) \mathcal{E}^{-1} s (\varphi(z)) \text{d}z \right]. \tag{3.2.60}
\]

Next, we apply the definition of the scaled coordinate to transform the integrals, i.e.,
\[
f^i_{j+1/2} = \Delta x \mathcal{E} \left( 2 \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \left[ \int_{0}^{1/2} \text{d}\sigma \sinh (\sigma \hat{D}) \mathcal{E}^{-1} s (\varphi(z(\sigma))) \text{d}\sigma \right.
\]
\[\left. - \int_{1/2}^{1} \text{d}\sigma \sinh \left( (1 - \sigma) \hat{D} \right) \mathcal{E}^{-1} s (\varphi(z(\sigma))) \text{d}\sigma \right]. \tag{3.2.61}
\]
3.2. System diffusion-reaction scheme

Alternatively, the inhomogeneous flux can be written as

\[ f^i_{j+1/2} = \Delta x \mathcal{E} \int_0^1 G \left( \sigma; \hat{D} \right) \mathcal{E}^{-1} s(\varphi(x(\sigma))) \, d\sigma, \]  

(3.2.62)

with \( G(\sigma; \hat{D}) \) the Green’s matrix relating the flux vector to the source term vector, and is given by

\[ G \left( \sigma; \hat{D} \right) = \left( 2 \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \begin{cases} \sinh \left( \sigma \hat{D} \right), & \text{for } 0 \leq \sigma \leq \frac{1}{2}, \\ -\sinh \left( (1-\sigma) \hat{D} \right), & \text{for } \frac{1}{2} < \sigma \leq 1. \end{cases} \]  

(3.2.63)

The Green’s matrix satisfies \( G(\frac{1}{2}^-; \hat{D}) - G(\frac{1}{2}^+; \hat{D}) = I \), i.e., the Green’s matrix is discontinuous for the diagonal elements at \( \sigma = \frac{1}{2} \) with jump 1, whereas the off-diagonal elements are continuous. These properties of the Green’s matrix were also found in [1], where the Green’s matrix is found for a system of advection-diffusion type equations.

The numerical inhomogeneous flux \( F^i_{j+1/2} \) can be derived by assuming that the source is constant within the control volume \( x_{j-1/2} < x < x_{j+1/2} \), i.e.,

\[ s(\varphi) = \begin{cases} s_j, & \text{for } x_{j-1/2} < x < x_{j+1/2}, \\ s_{j+1}, & \text{for } x_{j+1/2} < x < x_{j+3/2}. \end{cases} \]  

(3.2.64a)

Then, after diagonalizing the system again using the matrix \( \mathbf{V} \) the integrals can be evaluated and the system can be transformed back, resulting in

\[ F^i_{j+1/2} = \frac{\Delta x}{8} \mathcal{E} \tanh \left( \frac{1}{4} \hat{D} \right) \mathcal{E}^{-1} (s_j - s_{j+1}), \]  

(3.2.65)

where the function \( \tanh c(A) \) is defined by (3.2.12a) with \( g(z) = \tanh c(z) \).

In the limit that \( C = 0 \), then the inhomogeneous flux reduces to

\[ F^i_{j+1/2} = \frac{\Delta x}{8} (s_j - s_{j+1}). \]  

(3.2.66)

This is an additional inhomogeneous flux for the system central difference (CD) scheme.

3.2.3 Scheme overview

Now, that the homogeneous and inhomogeneous flux vectors have can been computed, we can summarise the resulting schemes. To recap, the flux balance for the system diffusion-reaction type conservation law is given by (3.2.4), and reads

\[ F_{j+1/2} - F_{j-1/2} = \Delta x \left( C_j \varphi_j + s_j \right). \]  

(3.2.67)

For the diffusion-reaction homogeneous flux (DR-HF) scheme, we only use the homogeneous flux given by (3.2.42), i.e.,

\[ F^h_{j+1/2} = \frac{\Delta x}{8} \mathcal{E} \left( \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} (\varphi_{j+1} - \varphi_j). \]  

(3.2.68a)

If additionally the inhomogeneous flux (3.2.65) is taken into account, then the scheme is referred to as the diffusion-reaction complete flux (DR-CF) scheme, i.e.,

\[ F^i_{j+1/2} = \frac{\Delta x}{8} \mathcal{E} \tanh \left( \frac{1}{4} \hat{D} \right) \mathcal{E}^{-1} (s_j - s_{j+1}). \]  

(3.2.69c)
These schemes can be compared with the system variant of the classical standard central difference (CD) scheme, where the numerical flux vector is given by (3.2.43), i.e.,

\[
F_{j+1/2}^h = F_{j+1/2},
\]

(3.2.70a)

\[
F_{j+1/2}^h = -\frac{1}{\Delta x} \mathcal{E} (\varphi_{j+1} - \varphi_j).
\]

(3.2.70b)

Note, that we do not take any inhomogeneous flux into account in the CD scheme.

### 3.2.4 Discrete mass and charge conservation

In a general multicomponent mixture consisting of \( m \) species where mass and charge should be conserved, the vectors \( 1^T \) and \( r^T \) should be left-eigenvectors of the discretisation matrices \( \mathcal{E} \) that appear in the numerical flux vector \( F_{j+1/2} \). The vectors \( 1 = (1, \ldots, 1)^T \) and \( r = (q_1/m_1, \ldots, q_m/m_m)^T \) are defined in section 2.4. In order to prove discrete mass and charge conservation, the diffusion and reaction matrices should have \( 1^T \) and \( r^T \) as left-eigenvectors. For the diffusion matrix \( \mathcal{E} \) it was already proven that the vectors \( 1^T \) and \( r^T \) are left-eigenvectors, see section 2.4. The corresponding eigenvalues are denoted by

\[
1^T \mathcal{E} = \epsilon^m 1^T, \quad (3.2.71a)
\]

\[
r^T \mathcal{E} = \epsilon^c r^T, \quad (3.2.71b)
\]

with the values given by

\[
\epsilon^m := \beta \sigma^m, \quad (3.2.72a)
\]

\[
\epsilon^c := \gamma r^T \rho_c. \quad (3.2.72b)
\]

Since no net mass or charge should be produced, the reaction matrix \( C \) should obey

\[
1^T C = 0^T, \quad (3.2.73a)
\]

\[
r^T C = 0^T. \quad (3.2.73b)
\]

The one-dimensional steady-state diffusion-reaction mass conservation law is given by

\[
-\frac{d}{dx} \left( \mathcal{E} \frac{dy}{dx} \right) = C y + s(y), \quad (3.2.74)
\]

with \( C y = \text{diag} (m) \omega \) the linear part of the reaction source term. The diffusion-reaction complete flux discretized scheme is given by

\[
-\alpha_{j-1/2} y_{j-1} + \left( \alpha_{j+1/2} + \beta_{j-1/2} \right) y_j - \beta_{j+1/2} y_{j+1} = \Delta x \left( C_j y_j + \gamma_{j-1/2} s_{j-1} + \left( I - \gamma_{j+1/2} + \delta_{j-1/2} \right) s_j - \delta_{j+1/2} s_{j+1} \right), \quad (3.2.75a)
\]

with the coefficient matrices \( \alpha_{j+1/2}, \beta_{j+1/2} \) etc. defined by

\[
\alpha_{j+1/2} := \frac{1}{\Delta x} \mathcal{E}_{j+1/2} \left( \sinhc \left( \frac{1}{2} \check{D}_{j+1/2} \right) \right)^{-1}, \quad \beta_{j+1/2} := \alpha_{j+1/2}
\]

\[
\gamma_{j+1/2} := \frac{1}{8} \mathcal{E}_{j+1/2} \tanhc \left( \frac{1}{4} \check{D}_{j+1/2} \right) \mathcal{E}^{-1}_{j+1/2}, \quad \delta_{j+1/2} := -\gamma_{j+1/2}. \quad (3.2.75b)
\]
For the first example we consider only the source $c\varphi$.

3.3.1 Example 1: homogeneous problem

and will not be mentioned hereafter.

In general this is a good practice to follow. Therefore, when computing numerical

or weighted averages over a control volume then describe the numerical flux instead of constant

advection and diffusion coefficients. This results into modified coefficients, i.e., arithmetic, harmonic

convergence are presented in the example.

If the exact solution is not available, then other methods for determining the accuracy and/or the

that the following relations hold for the coefficient matrices $\alpha$, $\beta$, $\gamma$.

Similarly, for the eigenvector $r^T$ we find

Therefore, premultiplying the discretized system with the eigenvectors $1^T$ and $r^T$ results in

where we have used $1^Ts_j = 0$ and $r^Ts_j = 0$, and defined $1^Ty_j =: \sigma^m_j$ and $r^Ty_j =: \sigma^c_j$ according to (2.1.10)-(2.2.16). From these relations and applying that the diffusive eigenvalues $\varepsilon^m_j$ and $\varepsilon^c_j$ are constant, i.e., $\varepsilon^m_{j+1/2} := \varepsilon^m$ and $\varepsilon^c_{j+1/2} := \varepsilon^c$ on each nodal point, it follows that $\sigma^m_j$ and $\sigma^c_j$ are weighted averages of its neighbours. Thus, when appropriate boundary conditions are applied such that $\sigma^m = 1$ and $\sigma^c = 0$ hold on the boundary, then the numerical solution obeys discrete mass and charge conservation without discretisation error.

3.3 Numerical examples: scalar scheme

In this section the scalar diffusion-reaction schemes are tested. The performance of the scalar DR-HF, DR-CF and CD schemes, described in section 3.1.3 are compared. In what follows, we will write the DR-HF as the HF scheme since the equations to be solved are diffusion-reaction equations. Similarly, for the DR-CF we write only CF.

The examples serve to verify the convergence and accuracy of the discretisation for a variety of problems. In general, the accuracy is quantified using the average discretisation error $\varepsilon(h) = ||\varphi - \varphi^*||_{\infty}$ with $\varphi = \varphi(x)$ the numerical solution and $\varphi^*$ the exact solution restricted to the grid. If the exact solution is not available, then other methods for determining the accuracy and/or the convergence are presented in the example.

In [2] and [6] the numerical flux for advection-diffusion schemes are computed with variable advection and diffusion coefficients. This results into modified coefficients, i.e., arithmetic, harmonic or weighted averages over a control volume then describe the numerical flux instead of constant coefficients. In general this is a good practice to follow. Therefore, when computing numerical solutions we interpolate the advection, diffusion and reaction coefficients to the interfaces using the arithmetic average. This interpolation is used in every numerical example throughout this thesis and will not be mentioned hereafter.

3.3.1 Example 1: homogeneous problem

For the first example we consider only the source $c\varphi(\bar{x})$, thus the BVP is given by

$$\varepsilon \frac{d^2 \varphi}{d\bar{x}^2} + c\varphi(\bar{x}) = 0, \quad 0 < \bar{x} < a, \quad (3.3.1a)$$

$$\varphi(0) = \varphi_L, \quad \varphi(a) = \varphi_R. \quad (3.3.1b)$$
The BVP can be made dimensionless by introducing the dimensionless coordinate \( x = \bar{x}/a \) and the diffusive Damköhler number \( Da := a^2 c/\varepsilon \), resulting in

\[
\frac{d^2 \varphi}{dx^2} + Da \varphi(x) = 0, \quad 0 < x < 1, \tag{3.3.2a}
\]

\[
\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R. \tag{3.3.2b}
\]

The analytical solution to this problem is given by

\[
\varphi(x) = \frac{\sinh((1 - x)\omega)\varphi_L + \sinh(\omega x)\varphi_R}{\sinh(\omega)}, \tag{3.3.3}
\]

where \( \omega := \sqrt{-Da} \).

In this example only the homogeneous flux (HF) and standard central difference (CD) schemes are compared, since there is no general source \( s(\varphi) \) present. We take \( \varphi_L = 0 \) and \( \varphi_R = 1 \). Typical solutions to this problem are plotted in figure 3.5. For increasing reaction, i.e. increasing \( |Da| \), the size of the boundary layer decreases. The discretisation errors are plotted in figures 3.6a-3.6d. From the figures it can be concluded that both the HF and CD schemes display second order convergence, while the HF scheme is in general slightly better than the CD scheme. In the case \( Da = -10^4 \) the discretisation error first increases for increasing number of gridpoints. This is due to the nature of the problem and the boundary layer not being represented well on the coarse grids. In the case \( Da = 10^4 \) a different type of behaviour is seen. The solution for this Damköhler number is not plotted in figure 3.5, however, it is simply a sinusoidal wave with wavelength \( \lambda = 2\pi/\sqrt{|Da|} \). Therefore, for \( h < 10^{-2} \) the gridspace requirement is satisfied. However, the HF scheme is more accurate than the CD scheme when \( h^{-1} = 320 \) or more gridpoints are used.

Furthermore, both the CD and HF scheme display second order convergence, while the discretisation error of the HF scheme is half of the error for CD scheme. This is confirmed in the figures and table 3.1, thus verifying the analytical derivation of the local discretisation error presented in section 3.1.5.

Figure 3.5: Example 1, homogeneous problem. Typical solutions for various Damköhler numbers \( Da \). Other parameters values are: \( \varphi_L = 0 \) and \( \varphi_R = 1 \).
3.3. Numerical examples: scalar scheme

Figure 3.6: Example 1, homogeneous problem. Discretization errors for various diffusive Damköhler numbers. Other parameters values are: \( \phi_L = 0 \) and \( \phi_R = 1 \).

Table 3.1: Example 1, homogeneous problem. Parameter values are: \( Da = -10^4 \), \( \phi_L = 0 \) and \( \phi_R = 1 \).

<table>
<thead>
<tr>
<th>( h )</th>
<th>( e_{CD}(h) )</th>
<th>( e_{CD}(h)/e_{CD}(h/2) )</th>
<th>( e_{DR}(h) )</th>
<th>( e_{DR}(h)/e_{DR}(h/2) )</th>
<th>( e_{CD}(h)/e_{DR}(h) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.759e-03</td>
<td>0.322</td>
<td>6.275e-04</td>
<td>0.068</td>
<td>15.552</td>
</tr>
<tr>
<td>20</td>
<td>3.035e-02</td>
<td>0.741</td>
<td>9.266e-03</td>
<td>0.492</td>
<td>3.276</td>
</tr>
<tr>
<td>40</td>
<td>4.096e-02</td>
<td>1.980</td>
<td>1.884e-02</td>
<td>1.832</td>
<td>2.175</td>
</tr>
<tr>
<td>80</td>
<td>2.069e-02</td>
<td>3.667</td>
<td>1.028e-02</td>
<td>3.649</td>
<td>2.012</td>
</tr>
<tr>
<td>160</td>
<td>5.642e-03</td>
<td>3.811</td>
<td>2.817e-03</td>
<td>3.806</td>
<td>2.002</td>
</tr>
<tr>
<td>320</td>
<td>1.480e-03</td>
<td>3.973</td>
<td>7.403e-03</td>
<td>3.973</td>
<td>2.000</td>
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<td>3.986</td>
<td>1.863e-04</td>
<td>3.986</td>
<td>2.000</td>
</tr>
<tr>
<td>1280</td>
<td>9.349e-05</td>
<td>3.998</td>
<td>4.675e-05</td>
<td>3.998</td>
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</tr>
<tr>
<td>2560</td>
<td>2.338e-05</td>
<td>1.169e-05</td>
<td></td>
<td></td>
<td>2.000</td>
</tr>
</tbody>
</table>
3.3.2 Example 2: linear source

For the second example we consider the following dimensionless BVP with a linear source

\[
\frac{d^2 \phi}{dx^2} + Da \phi(x) + s(x) = 0, \quad 0 < x < 1, \quad (3.3.4a)
\]
\[
s(x) = 4s_{\text{max}}x(1 - x), \quad (3.3.4b)
\]
\[
\phi(0) = \phi_L, \quad \phi(1) = \phi_R. \quad (3.3.4c)
\]

The analytical solution to this problem is given by

\[
\phi(x) = \left( \frac{\sinh(\omega(1 - x))}{\sinh(\omega)} + \frac{\sinh(\omega x)}{\sinh(\omega)} \right) \phi_L + \left( \frac{\sinh(\omega(1 - x))}{\sinh(\omega)} + \frac{\sinh(\omega x)}{\sinh(\omega)} \right) \phi_R
\]
\[
+ s_{\text{max}} \frac{8}{Da^2} \left( \frac{\sinh(\omega(1 - x)) + \sinh(\omega x)}{\sinh(\omega)} - 1 \right) - \frac{1}{Da} s(x), \quad (3.3.5)
\]

where \( \omega := \sqrt{-Da} \).

The numerical solutions are computed for various Damköhler numbers and are presented in figure 3.7. Furthermore, we have taken \( s_{\text{max}} = 10^4, \phi_L = 0 \) and \( \phi_R = 100 \). All three schemes display second order convergence. Moreover, the CD and HF scheme are comparable in accuracy when \( Da = +1 \), due to the low Damköhler number. The CF scheme is more accurate than the CD and HF scheme in both examples, due to the inclusion of the inhomogeneous flux.
3.3. Example 3: linear source with interior layer

In this example we will consider a source term with an interior layer, as defined in the following BVP

\[
\frac{d^2 \varphi}{dx^2} + Da (\varphi(x) + rs(x)) = 0, \quad 0 < x < 1, \tag{3.3.6a}
\]

\[
s(x) = \frac{s_{\text{max}}}{1 + s_{\text{max}} (2x - 1)^2}, \tag{3.3.6b}
\]

\[
\varphi(0) = 1, \quad \varphi(1) = 0. \tag{3.3.6c}
\]

Here, \( r \) represents an extra parameter to control the relative strength of \( Da \varphi(x) \) and \( Da rs(x) \), independent of the parameter \( s_{\text{max}} \). The source term has a sharp peak at \( x = \frac{1}{2} \), causing a peak for \( Da \ll -1 \) and a change in behaviour for \( Da \gg 1 \). These effects can be seen in figure 3.8. The change in amplitude of the oscillations in the first plot is caused by the source term. For the source parameter we take \( s_{\text{max}} = 10^3 \).

For this BVP there is no exact solution available. In order to determine the accuracy of the schemes, we compute numerical approximations of \( \varphi \left( \frac{1}{2} \right) \) for increasingly smaller grid sizes and apply

Figure 3.7: Example 2, linear source. Numerical and exact solutions (left), and the discretisation error (right). Parameter values are: \( s_{\text{max}} = 10^4 \), \( \varphi_L = 0 \) and \( \varphi_R = 100 \).
Richardson’s extrapolation to these results. Let

$$\varphi \left( \frac{1}{2} \right) = \varphi_h + e_h = \varphi_{h/2} + e_{h/2} = \varphi_{h/4} + e_{h/4}, \tag{3.3.7}$$

where $\varphi_h$ denotes the numerical approximation of $\varphi \left( \frac{1}{2} \right)$ computed with grid size $h$ and $e_h$ the corresponding (global) discretisation error. Assuming the following error expansion

$$e_h = Ch^p + O(h^q), \quad q > p, \tag{3.3.8}$$

we can determine the order of accuracy $p$ from:

$$2^p \cdot \frac{\varphi_{h/2} - \varphi_h}{\varphi_{h/4} - \varphi_{h/2}} =: r_h. \tag{3.3.9}$$

The $r_h$-values are reported in tables 3.2-3.4. All three schemes exhibit second order convergence. However, the numerical solutions in figure 3.8a show that the amplitude of the oscillations for the CD scheme are way too high for the coarse grid. The HF and CF schemes in these cases are already close to the numerical solution computed on the fine grid. In the second case, see figure 3.8b, there is not a large difference between the three used schemes on the coarse grid compared to the fine grid solution. In the last case, see figure 3.8c, the CD and HF schemes perform roughly equal, while the CF scheme has a better approximation of the peak value on the coarse grid.
3.3. Numerical examples: scalar scheme

Figure 3.8: Example 3, linear source with interior layer. Numerically obtained solutions for various Damköhler numbers. Parameter values are: $s_{\text{max}} = 10^3$.

<table>
<thead>
<tr>
<th>$h^{-1}$</th>
<th>$\tau_{\text{CD}}$</th>
<th>$\tau_{\text{HF}}$</th>
<th>$\tau_{\text{CF}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10.933</td>
<td>-0.787</td>
<td>-0.889</td>
</tr>
<tr>
<td>80</td>
<td>-0.203</td>
<td>-33.331</td>
<td>-29.113</td>
</tr>
<tr>
<td>160</td>
<td>4.898</td>
<td>4.229</td>
<td>4.036</td>
</tr>
<tr>
<td>320</td>
<td>3.965</td>
<td>3.998</td>
<td>3.952</td>
</tr>
<tr>
<td>640</td>
<td>3.978</td>
<td>3.996</td>
<td>3.984</td>
</tr>
<tr>
<td>1280</td>
<td>3.993</td>
<td>3.999</td>
<td>3.996</td>
</tr>
</tbody>
</table>
Table 3.3: Example 3, linear source with interior layer. Parameter values are: \(s_{\text{max}} = 10^3\), \(D_a = 10^2\) and \(r = 10^{-2}\).

<table>
<thead>
<tr>
<th>(h^{-1})</th>
<th>(r_{\text{CD},h})</th>
<th>(r_{\text{HF},h})</th>
<th>(r_{\text{CF},h})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12.196</td>
<td>9.005</td>
<td>8.486</td>
</tr>
<tr>
<td>40</td>
<td>-2.619</td>
<td>-10.158</td>
<td>-12.888</td>
</tr>
<tr>
<td>80</td>
<td>3.557</td>
<td>3.194</td>
<td>3.064</td>
</tr>
<tr>
<td>160</td>
<td>4.006</td>
<td>4.022</td>
<td>4.023</td>
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<tr>
<td>320</td>
<td>4.001</td>
<td>4.005</td>
<td>4.006</td>
</tr>
<tr>
<td>640</td>
<td>4.000</td>
<td>4.001</td>
<td>4.001</td>
</tr>
</tbody>
</table>

Table 3.4: Example 3, linear source with interior layer. Parameter values are: \(s_{\text{max}} = 10^3\), \(D_a = -10^2\) and \(r = -10^{-2}\).

<table>
<thead>
<tr>
<th>(h^{-1})</th>
<th>(r_{\text{CD},h})</th>
<th>(r_{\text{HF},h})</th>
<th>(r_{\text{CF},h})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.482</td>
<td>2.530</td>
<td>2.460</td>
</tr>
<tr>
<td>20</td>
<td>5.734</td>
<td>5.738</td>
<td>6.979</td>
</tr>
<tr>
<td>40</td>
<td>12.730</td>
<td>12.437</td>
<td>-54.597</td>
</tr>
<tr>
<td>80</td>
<td>5.398</td>
<td>5.335</td>
<td>1.465</td>
</tr>
<tr>
<td>160</td>
<td>4.087</td>
<td>4.084</td>
<td>3.849</td>
</tr>
<tr>
<td>320</td>
<td>4.020</td>
<td>4.019</td>
<td>3.966</td>
</tr>
</tbody>
</table>

3.3.4 Example 4: non-linear source

Consider the following problem

\[
\frac{1}{2} \frac{d^2 \varphi(x)}{dx^2} = \varphi^3(x) - 3a\varphi(x) - x^3 + a \frac{1 - a^2}{x^3}, \quad 1 < x < 2, \quad (3.3.10a)
\]

\[
\varphi(1) = a + 1, \quad \varphi(2) = \frac{a}{2} + 2. \quad (3.3.10b)
\]

The analytical solution is given by

\[
\varphi(x) = \frac{a}{x} + x. \quad (3.3.11)
\]

The cases where \(a = \pm 1\) are investigated, such that the last term of the source is equal to 0. For solution method we use Newton iteration. The iteration process is stopped when \(||\delta \varphi||_\infty < \text{tol}\) and \(||F||_\infty < \text{tol}\). Here, \(\delta \varphi\) contains the update value at each nodal point after an iteration and \(||F||_\infty = ||A\varphi - b||_\infty\) is the residual. For the tolerance we set \(\text{tol} = 10^{-12}\).

For \(a = 1\) the solutions are plotted in figure 3.9. For this coarse grid, \(h^{-1} = 10\), the numerical solution is hardly distinguishable from the exact solution. All three schemes show second order convergence behaviour. However, the CD scheme performs slightly better than the HF and CF scheme, while we would expect the CF scheme to be more accurate since it takes into account the source term in the inhomogeneous flux.
3.3. Numerical examples: scalar scheme

For $a = -1$ the solutions are plotted in figure 3.10. Again for this coarse grid the numerical solution is hardly distinguishable from the exact solution and all three schemes show second order convergence behaviour. In contrast to the case where $a = 1$, now the CF scheme is clearly more accurate than the CD and HF schemes.

3.3.5 Example 5: diffusion profile

Consider the following problem

$$\frac{d}{dx} \left( \frac{1}{Da_0} (\alpha x + 1)^2 \frac{d\varphi}{dx} \right) + \varphi(x) = 0, \quad 0 < x < 1, \quad (3.3.12a)$$

$$\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R. \quad (3.3.12b)$$

Here, $Da_0 < 0$ is a constant Damköhler number that represents the usual reaction over transport. However, the diffusion in this problem is spatially dependent, therefore whether reaction is dominant will also depend on the coordinate. The analytical solution to this problem can be found with the
substitution $e^\theta = \alpha x + 1$, i.e., the ODE is transformed to
\[
\frac{\alpha^2}{Da_0} \left( \frac{d^2 \varphi}{d\theta^2} + \frac{d\varphi}{d\theta} \right) + \varphi(\theta) = 0.
\]

The analytical solution of this ODE is given by
\[
\varphi(\theta) = A (\exp(\theta))^{-\frac{1}{2}(1-r)} + B (\exp(\theta))^{-\frac{1}{2}(1+r)},
\]
with $r = \sqrt{1 - 4\alpha^{-2} Da_0}$. After transforming back and applying boundary conditions, we find
\[
\varphi(x) = A (\alpha x + 1)^{-\frac{1}{2}(1-r)} + B (\alpha x + 1)^{-\frac{1}{2}(1+r)},
\]
with
\[
A = \frac{\varphi_R (\alpha + 1)^{\frac{1}{2}(1+r)} - \varphi_L}{(\alpha + 1)^{\frac{1}{2}(1+r)} - 1},
\]
\[
B = \varphi_L - A.
\]

In this example we set $Da_0 = -2 \cdot 10^3$ and boundary conditions $\varphi_L = \varphi_R = 10$. First of all, we set $\alpha = 40$ such that at the left boundary the problem is reaction dominant and on the right boundary diffusion is dominant. The solution $\varphi(x)$ and discretisation error $e_h(h)$ are plotted in figure 3.11. Both the CD and HF scheme, on a coarse grid, show discrepancies between the exact solution and the numerical solution at the left boundary where a large gradient is present due to reaction being dominant. However, the HF scheme performs slightly better than the CD scheme. This is confirmed in figure 3.11b, moreover both schemes show second order convergence.

Next, we set $\alpha = 1$ such that the diffusion does not change much over the domain, therefore we expect the solution to be reaction dominant with boundary layers on both sides. The solution $\varphi(x)$ and the discretisation error $e_h(h)$ are plotted in figure 3.12. On the coarse grid both schemes can accurately capture the exact solution. Furthermore, the HF schemes performs better than the CD scheme by a factor $\frac{1}{2}$ as expected from theory.
Figure 3.12: Example 5b, reaction dominant solution. Here $D_0 = -2 \cdot 10^3$ and $\alpha = 1$.

To further investigate why in the first case the HF scheme is only slightly better than the CD scheme, we show the difference between the numerical solution and exact solution for both cases. The difference is given by $\varphi(x) - \varphi^*(x)$ where $\varphi^*(x)$ is the exact solution restricted to the grid. The result is plotted in figure 3.13. For the case $\alpha = 40$, the minimum of the numerical solutions are displaced compared to the exact solution. This is confirmed in figure 3.13. This displaced peak is the main cause for the discretisation error and occurs for both schemes, therefore both schemes display comparable accuracy. For the case $\alpha = 1$, the variation in the diffusion coefficient is more gentle and thus the schemes can more accurately capture the behaviour near the left wall. Therefore, the advantage of the HF scheme is visible in this case.

Figure 3.13: Example 5, the difference between the numerical solution and exact solution, i.e., $\varphi(x) - \varphi^*(x)$. Here $D_0 = -2 \cdot 10^3$ and $h^{-1} = 20$. 
3.3.6 Example 6: steep boundary layer

Consider the following dimensionless BVP

$$-\frac{d^2\varphi}{dx^2} = Da \varphi(x) + s(x), \quad 0 < x < 1,$$

$$\varphi(0) = 0, \quad \varphi(1) = 1.$$ (3.3.14a)

We construct a synthesized solution by substituting the following exact solution in the ODE:

$$\varphi(x) = 2\exp(x) - \exp\left(-\frac{x}{\delta}\right)\exp(1) - \exp\left(-\frac{1}{\delta}\right) - Da x^3 - \frac{6x}{Da-6}.$$ (3.3.15)

Then, we obtain the following expression for the source term $s(x)$

$$s(x) = \frac{\exp(x) - \frac{1}{\delta} \exp(-x/\delta)}{\exp(1) - \exp(1/\delta)} - Da \left(\frac{\exp(x) - \exp(-x/\delta)}{\exp(1) - \exp(1/\delta)} - \frac{Da x^3}{Da-6}\right).$$ (3.3.16)

Here, $\delta$ estimates the size of the boundary layer on the left side of the domain.

In the case where $|Da| \gg 1$, reaction is dominant and the solution is given by

$$\varphi(x) = 2\exp(x) - \exp\left(-\frac{x}{\delta}\right)\exp(1) - \exp\left(-\frac{1}{\delta}\right) - Da x^3,$$ (3.3.17)

while if $|Da| \ll 1$, diffusion is dominant and therefore the solution is given by

$$\varphi(x) = 2\exp(x) - \exp\left(-\frac{x}{\delta}\right)\exp(1) - \exp\left(-\frac{1}{\delta}\right) - x.$$ (3.3.18)

In this example we set $\delta = 10^{-2}$ such that the source has a steep gradient near $x = 0$. First we consider the problem for the $Da = -10^2$. The numerical and exact solutions, and discretisation errors $e_h(h)$ are shown in figure 3.14. The discretisation error plot shows that the CF scheme performs better than the HF and CD scheme. All three schemes show second order convergence behaviour, however, note that for very coarse grids the CF scheme performs worse than CD and HF schemes.

![Numerical Solution and Discretisation Error](image_url)

(a) numerical solution for $h^{-1} = 40$  
(b) discretisation error

Figure 3.14: Example 6a, steep boundary layer. Here Da = $-10^2$ and $\delta = 10^{-2}$.

Next, we decrease the Damkohler number four orders of magnitude to $Da = -10^{-2}$. The numerical solutions and discretisation error are plotted in figure 3.15. The numerical solutions show
large discrepancies in the boundary layer, where both the CD and HF schemes undershoot the value while the CF scheme overshoots. For this case again the CF scheme performs better than the CD and HF schemes for grid sizes sufficiently fine such that the numerical solution is a good approximation of the exact solution.

![Graphs](image)

(a) numerical solution for $h^{-1} = 40$

(b) discretisation error

Figure 3.15: Example 6b, steep boundary layer. Here $Da = -10^{-2}$ and $\delta = 10^{-2}$.

### 3.4 Numerical examples: system scheme

In this section the performance of the system DR-HF scheme, described in section 3.2.3, is compared with the system variant of the CD scheme. The examples serve to verify the convergence and accuracy of the discretisation for a variety of problems. In general, the accuracy is quantified using the average discretisation error $e_i(h) = ||\varphi_i - \varphi_i^*||_\infty$ with $\varphi_i = \varphi_i(x)$ the numerical solution and $\varphi_i^*$ the exact solution restricted to the grid.

#### 3.4.1 Example 1: coupled system

Consider the following dimensionless system BVP

\[
\begin{align*}
\frac{d^2\varphi}{dx^2} + Da^d \varphi & = 0, \quad 0 < x < 1 \\ \varphi(0) & = \varphi_L, \quad \varphi(1) = \varphi_R,
\end{align*}
\]  

(3.4.1a)

with $Da^d$ the diffusive Damköhler matrix. The diffusive Damköhler matrix is found from a diffusion matrix $E$ and reaction matrix $C$ given by

\[
E = \frac{1}{2} \varepsilon \begin{pmatrix} 1 + \alpha & 1 - \alpha \\ 1 - \alpha & 1 + \alpha \end{pmatrix}, \quad C = k \text{ diag}(1, r),
\]  

(3.4.2)

and an appropriate length scale $a$. Then, the Damköhler matrix reads

\[
Da^d = E^{-1}Ca^2 = d \begin{pmatrix} 1 + \alpha & r(1 - \alpha) \\ -1 + \alpha & r(1 + \alpha) \end{pmatrix},
\]  

(3.4.3)

where $d = \frac{1}{2} ka^2/(\alpha \varepsilon)$ is a diffusive Damköhler number. The solution of the system BVP (3.4.1) reads

\[
\varphi(x) = \left(\sinh \left(\sqrt{-Da^d}\right)\right)^{-1} \left(\sinh \left(\sqrt{-Da^d} (1 - x)\right) \varphi_L + \sinh \left(\sqrt{-Da^d} x\right) \varphi_R\right).
\]  

(3.4.4)
We take the following parameters \( d = -2.5 \cdot 10^3 \), \( \alpha = 0.2 \) and \( r = 10^{-3} \). For the boundary conditions we use \( \varphi_L = (0.2, 0.8)^T \) and \( \varphi_R = (0.6, 0.4)^T \). For \( \varphi_1(x) \) the solution is reaction dominant, while for \( \varphi_2(x) \) reaction and diffusion are balanced. The solutions, however, are strongly coupled through the diffusion matrix. The numerical solutions and discretisation errors are shown in figure 3.16. For both variables \( \varphi_1(x) \) the solutions show boundary layers near both boundaries. For \( \varphi_2(x) \) the boundary layer is present due to the coupling with \( \varphi_1(x) \). Both the DR-HF and CD scheme display second order convergence, with the DR-HF scheme being slightly more accurate than the CD scheme, similar to the scalar variant of the problems.

![Figure 3.16: Example 1: coupled diffusion-reaction system. Numerical solutions and corresponding discretisation error. Parameter values are \( d = -2.5 \cdot 10^3 \), \( \alpha = 0.2 \) and \( r = 10^{-3} \).](image)

3.4.2 Example 2: oscillatory solutions

Again, we consider the system BVP (3.4.1) where we now replace the Dirichlet boundary condition on the left-hand side with a homogeneous Neumann boundary condition, i.e.,

\[
\left. \frac{d\varphi}{dx} \right|_{x=0} = 0. \tag{3.4.5}
\]

Weak coupling

First, we take the parameters \( d = 187.5 \), \( \alpha = 0.8 \) and \( r = 0.03 \). Since the reaction terms are positive and there is a weak coupling, we expect a superposition of oscillations in the solution. The analytical solution reads

\[
\varphi(x) = \left( \cos \left( \sqrt{D}a^d \right) \right)^{-1} \cos \left( \sqrt{D}a^d x \right) \varphi_R. \tag{3.4.6}
\]

An example of the numerical solutions and corresponding discretisations errors are shown in figure 3.17. The oscillations clearly are a superposition of two oscillations as expected. Furthermore, the DR-HF and CD scheme both display second order convergence, with the DR-HF scheme being slightly more accurate. The peaks in the discretisation error are due to the inadequate number of gridpoints used for representing the oscillations.
3.4. Numerical examples: system scheme

Figure 3.17: Example 1: oscillatory solutions with weak coupling. Numerical solutions and corresponding discretisation error. Parameter values are \( d = 187.5 \), \( \alpha = 0.8 \) and \( r = 0.03 \).

**Strong coupling**

Next, we change the coupling parameter such that \( d = 750 \) and \( \alpha = 0.2 \). The oscillations are now more strongly coupled and due to the increase of the Damköhler number we expect a higher frequency. This is confirmed in the figure 3.18. The high oscillatory behaviour of \( \varphi_1(x) \) is more present in the solution \( \varphi_2(x) \) due to the higher coupling coefficient. Again, the DR-HF and CD scheme both display second order convergence, with the DR-HF scheme being slightly more accurate.

Figure 3.18: Example 1: oscillatory solutions with strong coupling. Numerical solutions and corresponding discretisation error. Parameter values are \( d = 750 \), \( \alpha = 0.2 \) and \( r = 0.03 \).

3.4.3 Example 3: zero eigenvalue

In this example we construct the numerical solution for a diffusive Damköhler matrix with one eigenvalue equal to 0. Therefore, consider the following Damköhler matrix

\[
Da^d = d \begin{pmatrix} 0 & 1 \\ 0 & r \end{pmatrix}. \tag{3.4.7}
\]
The solution vector $\varphi(x)$ will thus be a superposition of a linear profile and a sinh$(x)$ or sin$(x)$ profile, depending on the sign of $dr$. The exact solution reads

$$\varphi(x) = \begin{pmatrix} 1 & r^{-1} \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha_1 x + \beta_1 \\ \alpha_2 e^{\omega x} + \beta_2 e^{-\omega x} \end{pmatrix},$$

(3.4.8)

where $\omega := \sqrt{-dr}$. The coefficients $\alpha_i$, $\beta_i$ for $i = 1, 2$ have to be determined from the following Dirichlet boundary conditions

$$\varphi_L = (0,1)^T \quad \varphi_R = (1,0)^T.$$  

(3.4.9)

We take the parameters $d = -30$ and $r = 10$. The resulting numerical solutions are shown in figure 3.19. The homogeneous flux derived in section 3.2.1 is shown to be still valid in case one eigenvalue is equal to 0. The numerical solution shows that $\varphi_1(x)$ is linear except near the left boundary, where the solution of $\varphi_2(x)$ is still large enough to impact $\varphi_1(x)$. The DR-HF scheme is more accurate than the CD scheme, while both display second order convergence.

![Numerical Solutions and Discretisation Errors](image)

(a) numerical solutions $\varphi(x)$ for $h^{-1} = 40$  
(b) discretisation errors $e_i(h)$

Figure 3.19: Example 1: coupled diffusion-reaction system. Numerical solutions and corresponding discretisation error. Parameter values are $d = -30$ and $r = 10$. 
Chapter 4

FVM applied to advection-diffusion-reaction equations

In this chapter the focus is on deriving flux approximation schemes for conservation laws of advection-diffusion-reaction type, where reaction indicates a linear reaction term. The flux will be approximated by a numerical flux computed from a local solution of the relevant boundary value problem. As will be shown in this chapter, the numerical flux will consist of a homogeneous and an inhomogeneous flux. If only the homogeneous flux is considered, then the scheme is referred to as the advection-diffusion-reaction homogeneous flux (ADR-HF) scheme. If both the homogeneous and inhomogeneous fluxes are considered, then the scheme is referred to as the advection-diffusion-reaction complete flux (ADR-CF) scheme. These schemes will be compared with the advection-diffusion homogeneous flux (AD-HF) and advection-diffusion complete flux (AD-CF) schemes, presented in [1].

First, a summary of the flux approximation schemes for the scalar advection-diffusion-reaction conservation law from [7] is given in section 4.1. Next, the scheme is extended to a system of conservation laws of advection-diffusion-reaction type in section 4.2, where the coupling of the individual equations is taken into account. Then, the performances of the scalar scheme and system scheme are tested for several test problems in sections 4.3 and 4.4, respectively.

4.1 Scalar advection-diffusion-reaction scheme

In [7] by J.H.M. ten Thije Boonkkamp et al. the numerical flux approximation schemes were already derived for this type of scalar conservation law. In this section only a summary of the results are presented. The FVM is applied to the following one-dimensional scalar advection-diffusion-reaction problem

\[ \frac{d}{dx} \left( u \varphi - \varepsilon \frac{d \varphi}{dx} \right) = c \varphi + s(\varphi), \quad (4.1.1) \]

where \( u \) is the advection coefficient, \( \varepsilon \) is the diffusion coefficient and \( c \varphi + s(\varphi) \) denotes the complete source term, with \( c \varphi \) the linear part of the source term. The flux is defined as

\[ f := u \varphi - \varepsilon \frac{d \varphi}{dx}, \quad (4.1.2) \]

therefore ODE (4.1.1) can be written as

\[ \frac{df}{dx} = c \varphi + s(\varphi). \quad (4.1.3) \]
and reaction coefficient $c$

The homogeneous ODE is given by

$$4.1.1 \text{ Homogeneous flux}$$

F_{j+1/2} - F_{j-1/2} = \Delta x \left(c_j \varphi_j + s_j\right), \quad (4.1.5)

where $c_j := c(x_j)$, $\varphi_j := \varphi(x_j)$ and $s_j := s(\varphi_j)$. The numerical flux $F_{j+1/2}$ is determined from the local boundary value problem (BVP) with constant advection coefficient $u$, diffusion coefficient $\varepsilon$ and reaction coefficient $c$, i.e.,

$$u \frac{d\varphi}{dx} - \varepsilon \frac{d^2\varphi}{dx^2} = c\varphi + s(\varphi), \quad x_j < x < x_{j+1}, \quad (4.1.6a)$$

$$\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}. \quad (4.1.6b)$$

The numerical flux will consist of a homogeneous flux and an inhomogeneous flux, i.e., $F_{j+1/2} = F_{j+1/2}^h + F_{j+1/2}^i$. First, the results of [7] for the homogeneous flux $F_{j+1/2}^h$ are shown in section 4.1.1. Followed by the results for the inhomogeneous flux $F_{j+1/2}^i$, which were presented with integrals in [7]. The integrals are approximated in section 4.1.2.

### 4.1.1 Homogeneous flux

The homogeneous ODE is given by

$$u \frac{d\varphi}{dx} - \varepsilon \frac{d^2\varphi}{dx^2} = c\varphi, \quad (4.1.7)$$

for which the characteristic equation reads $\varepsilon \lambda^2 - u\lambda + c = 0$ with discriminant $\Delta = u^2 - 4\varepsilon c$. The following auxiliary variables are introduced

$$d := \frac{\varepsilon c}{u^2}, \quad P := \frac{u\Delta x}{\varepsilon}, \quad D := \frac{|c| (\Delta x)^2}{\varepsilon}, \quad (4.1.8)$$

where $P$ is the Péclet number and $D$ the Damköhler number. Note that $d = \text{sgn}(c)D/P^2$, i.e., it is a parameter measuring the Damköhler-Péclet ratio. Furthermore, the following auxiliary functions are defined

$$B(z) := \frac{z}{e^z - 1}, \quad (4.1.9)$$

$$W(z) := \frac{e^z - z - 1}{z (e^z - 1)}, \quad (4.1.10)$$

$$W_1(z) := \frac{e^{-z/2} - 1 + \frac{z}{2}}{z(1 - e^{-z})}. \quad (4.1.11)$$

The functions are plotted in figure 4.1.

By solving the homogeneous BVP (4.1.6), i.e., $s(\varphi) = 0$, and subsequently computing the numerical flux using (4.1.2), the following homogeneous fluxes can be found. Three different cases have to be considered. First, for $Z > 0 \leftrightarrow d < \frac{1}{4}$, the characteristic equation has two distinct real roots $\lambda = u(1 \pm r)/(2\varepsilon)$ with $r = \sqrt{1 - 4d}$. The homogeneous flux is given by

$$F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} \left(C(P; r)B(-Pr)\varphi_j - C(-P; r)B(Pr)\varphi_{j+1}\right), \quad (4.1.12a)$$

$$C(P; r) = e^{P(1-2r)/4} \left( \cosh \left( \frac{1}{4} Pr \right) + \frac{1}{4} P \sinh \left( \frac{1}{4} Pr \right) \right). \quad (4.1.12b)$$
4.1. Scalar advection-diffusion-reaction scheme

The homogeneous flux is reminiscent of the advection-diffusion homogeneous flux [1, 2], with correction factors $C(P; r)$ and $C(-P; r)$. The advection-diffusion homogeneous flux and complete flux schemes will also be described in section 4.1.4.

Second, for $Z = 0$, and hence $d = \frac{1}{4}$ and $r = 0$, the characteristic equation has the double real root $\lambda = u/(2\varepsilon)$. The homogeneous flux is given by

$$F_{j+1/2}^h = \frac{\varepsilon}{\Delta x}(C(P)\varphi_j - C(-P)\varphi_{j+1}), \quad (4.1.13a)$$

$$C(P) = e^{P/4} \left(1 + \frac{1}{4}P\right). \quad (4.1.13b)$$

Third, for $Z < 0$ or equivalently $d > \frac{1}{4}$, the characteristic equations has two complex roots $\lambda = u(1 \pm ir)/(2\varepsilon)$ with $r = \sqrt{4d - 1}$. The homogeneous flux is given by

$$F_{j+1/2}^h = \frac{\varepsilon}{\Delta x}(C(P; r)\varphi_j - C(-P; r)\varphi_{j+1}), \quad (4.1.14a)$$

$$C(P; r) = e^{P/4} \cos \left(\frac{1}{4}Pr\right) + \frac{1}{4}P \sin \left(\frac{1}{2}Pr\right) \sin \left(\frac{1}{2}Pr\right). \quad (4.1.14b)$$

This expression is valid provided $\frac{1}{2} |P| r < \pi$. This restriction is similar to the one for the diffusion-reaction system described in section 3.1.4.

Alternatively, the expressions for $Z = 0$ and $Z < 0$ follow directly from (4.1.12) if we let $r = \sqrt{1 - 4d}$ be imaginary for $Z < 0$.

4.1.2 Inhomogeneous flux

In [7] by J.H.M. ten Thije Boonkkamp et al. the inhomogeneous flux for the advection-diffusion-reaction equation with linear source term is only presented as an integral. This inhomogeneous flux is given by equation [7, eq. (22)] and is presented here again. However, first we will elaborate on the derivation of the inhomogeneous flux.

The complete BVP (4.1.16) is reformulated as the first order ODE-system

$$q' = Aq + b, \quad x_j < x < x_{j+1}, \quad (4.1.15a)$$

$$\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}, \quad (4.1.15b)$$
where \( q, A \) and \( b \) are given by

\[
q = \begin{pmatrix} \varphi \end{pmatrix}, \quad A = \begin{pmatrix} \varepsilon^{-1} u & -\varepsilon^{-1} \\ c & 0 \end{pmatrix}, \quad b = \begin{pmatrix} 0 \\ s(\varphi) \end{pmatrix},
\]

(4.1.15c)

Here the prime \( ' \) denotes \( \frac{d}{dx} \). The fundamental matrix

\[
Q = \begin{pmatrix} \varphi_1 & \varphi_2 \\ f_1 & f_2 \end{pmatrix}
\]

(4.1.16)

corresponding to [4.1.15] satisfies the BVP

\[
Q' = AQ, \quad x_j < x < x_{j+1},
\]

\[
\varphi_1(x_j) = 1, \varphi_1(x_{j+1}) = 0, \quad \varphi_2(x_j) = 0, \varphi_2(x_{j+1}) = 1.
\]

(4.1.17a, b)

Here, \( \varphi_1(x), \varphi_2(x), f_1(x), f_2(x) \) denote the fundamental solutions. The fundamental solutions \( \varphi_1(x) \) and \( \varphi_2(x) \), for \( D > 0 \), are given by

\[
\varphi_1(x) = e^{P\sigma(x)/2} \sinh \left( \frac{1}{2} Pr (1 - \sigma(x)) \right) \sinh \left( \frac{1}{2} Pr \right),
\]

(4.1.18a)

\[
\varphi_2(x) = e^{-P(1-\sigma(x))/2} \sinh \left( \frac{1}{2} Pr \sigma(x) \right) \sinh \left( \frac{1}{2} Pr \right),
\]

(4.1.18b)

with \( \sigma(x) = (x - x_j)/\Delta x \) the scaled coordinate. Applying variation of constants, results in [7 eq. (19)-(22)]:

\[
q(x) = Q(x) r + \int_{x_j}^{x_{j+1}} G(x; y) b(y) dy, \quad r = \begin{pmatrix} \varphi_j \\ \varphi_{j+1} \end{pmatrix},
\]

(4.1.19)

with \( G(x; y) \) the Green’s function given by

\[
G(x; y) = (\varepsilon W(\varphi_1, \varphi_2)(y))^{-1} \begin{pmatrix} -\varphi_1(x)f_2(y) & \varphi_1(x)\varphi_2(y) \\ -f_1(x)f_2(y) & f_1(x)\varphi_2(y) \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix}
\]

for \( x_j \leq y \leq x \),

\[
\begin{pmatrix} -\varphi_2(x)f_1(y) & \varphi_2(x)\varphi_1(y) \\ -f_2(x)f_1(y) & f_2(x)\varphi_1(y) \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix}
\]

for \( x < y \leq x_{j+1} \).

(4.1.20)

Here, \( W(\varphi_1, \varphi_2) \) is the Wronskian of \( \varphi_1 \) and \( \varphi_2 \), which is given by

\[
W(\varphi_1, \varphi_2) = \begin{vmatrix} \varphi_1 & \varphi_2 \\ \varphi'_{\varphi_1} & \varphi'_{\varphi_2} \end{vmatrix} = \frac{1}{\Delta x} \frac{e^{P(\sigma(\varphi))^{1/2}}}{\sinh \left( \frac{1}{2} Pr \right)}.
\]

(4.1.21)

The inhomogeneous flux \( f^i(x_{j+1/2}) \) is the second component of the inhomogeneous term in [4.1.19] evaluated at \( x_{j+1/2} \) and reads

\[
f^i(x_{j+1/2}) = \frac{1}{\varepsilon} F_{i,j+1/2} h \int_{x_j}^{x_{j+1/2}} \frac{\varphi_2(x)s(x)}{W(\varphi_1, \varphi_2)(x)} \, dx
\]

\[
+ \frac{1}{\varepsilon} F_{i,j+1/2} h \int_{x_{j+1/2}}^{x_{j+1}} \frac{\varphi_1(x)s(x)}{W(\varphi_1, \varphi_2)(x)} \, dx.
\]

(4.1.22)

Here, \( F_{i,j+1/2} \) are the flux values corresponding to \( f_i(x) \) and can readily be found from [4.1.12] by substituting \( \varphi_j = 1, \varphi_{j+1} = 0 \) or \( \varphi_j = 0, \varphi_{j+1} = 1 \), for \( i = 1, 2 \), respectively.

Next, the numerical inhomogeneous flux \( F^i_{j+1/2} \) can be derived by assuming that the source is constant in the control volume \( x_{j-1/2} < x < x_{j+1/2} \), i.e.,

\[
s(\varphi) = \begin{cases} s_j, & \text{for } x_{j-1/2} < x < x_{j+1/2}, \\ s_{j+1}, & \text{for } x_{j+1/2} < x < x_{j+3/2}. \end{cases}
\]

(4.1.23a)
Then, the numerical inhomogeneous flux reads

\[ F^i_{j+1/2} = \frac{1}{\varepsilon} F^h_{j+1/2} I_1 s_j + \frac{1}{\varepsilon} F^h_{j+1/2} I_2 s_{j+1}, \quad \text{(4.1.24)} \]

where the following integrals need to be evaluated

\[ I_1 := \int_{x_j}^{x_{j+1/2}} \frac{\varphi_2(x)}{W(\varphi_1, \varphi_2)(x)} dx, \quad \text{(4.1.25a)} \]

\[ I_2 := \int_{x_{j+1/2}}^{x_{j+1}} \frac{\varphi_1(x)}{W(\varphi_1, \varphi_2)(x)} dx. \quad \text{(4.1.25b)} \]

Starting with the integral \( I_1 \), we will first substitute the expressions for \( \varphi_2(x) \) and the Wronskian \( W(\varphi_1, \varphi_2) \), then rewrite the integral to the scaled coordinate \( \sigma(x) \), followed by evaluation of the integral:

\[ I_1 = \int_{x_j}^{x_{j+1/2}} \frac{\varphi_2(x)}{W(\varphi_1, \varphi_2)(x)} dx \]

\[ = \Delta x \int_{x_j}^{x_{j+1/2}} e^{-P(1-\sigma(x))/2} \sinh \left( \frac{1}{2} Pr \sigma(x) \right) \sinh \left( \frac{1}{2} Pr \right) \frac{\sinh \left( \frac{1}{2} Pr \sigma(x)-1/2 \right)}{e^{P(\sigma(x)-1/2)}} dx \]

\[ = \Delta x^2 \int_{0}^{1/2} \sinh \left( \frac{1}{2} Pr \sigma \right) e^{-P(1-\sigma)/2} \frac{\sinh \left( \frac{1}{2} Pr \right)}{e^{P(\sigma-1/2)}} d\sigma \]

\[ = \Delta x^2 \frac{1}{Pr} \int_{0}^{1/2} \left( e^{P(\sigma-1)\sigma/2} - e^{-P(\sigma+1)\sigma/2} \right) d\sigma \]

\[ = \frac{\Delta x^2}{Pr} \left[ \frac{e^{P(\sigma-1)\sigma/2}}{P(r-1)/2} + \frac{e^{-P(\sigma+1)\sigma/2}}{P(r+1)/2} \right]_0 \]

\[ = \frac{2\Delta x^2}{P^2 r(r^2-1)} \left[ e^{-P/4} \left( (r+1)e^{Pr/4} + (r-1)e^{-Pr/4} \right) - 2r \right] \]

\[ = \frac{4\Delta x^2}{P^2 r(r^2-1)} \left[ e^{-P/4} \left( \sinh \left( \frac{1}{4} Pr \right) + r \cosh \left( \frac{1}{4} Pr \right) \right) - r \right] \]

\[ = \frac{4\Delta x^2}{P^2 r(r^2-1)} \left[ e^{-P/4} \left( \frac{1}{4} Pr \sinh \left( \frac{1}{4} Pr \right) + \cosh \left( \frac{1}{4} Pr \right) \right) - 1 \right]. \quad \text{(4.1.26)} \]
Similarly, for $I_2$ we find:

$$I_2 = \int_{x_{j+1/2}}^{x_{j+1}} \Phi(x) \, dx$$

$$= \Delta x \int_{x_{j+1/2}}^{x_{j+1}} e^{P\sigma(x)/2} \sinh \left( \frac{1}{2} P r (1 - \sigma(x)) \right) \sinh \left( \frac{1}{2} P r \right) \frac{e^{P\sigma(x)/2}}{e^{P\sigma(x/2)}} \, dx$$

$$= \Delta x^2 \int_{1/2}^{1} \sinh \left( \frac{1}{2} P r (1 - \sigma) \right) \frac{e^{P\sigma/2}}{e^{P\sigma(x/2)}} \, d\sigma$$

$$= \frac{\Delta x^2}{P r} e^{P/2} \int_{1/2}^{1} \sinh \left( \frac{1}{2} P r (1 - \sigma) \right) e^{-P\sigma/2} \, d\sigma$$

$$= \frac{\Delta x^2}{P r} e^{P/2} \left[ -\frac{e^{-P/2}}{r+1} - \frac{e^{-P/2}}{r-1} + \frac{e^{P(r+1)/4}}{r+1} + \frac{e^{-P(r+1)/4}}{r-1} \right]^{1/2}$$

$$= \frac{2\Delta x^2}{P^2 r (r^2 - 1)} \left[ e^{P/4} (r-1)e^{Pr/4} + (r+1)e^{-Pr/4} - 2r \right]$$

$$= \frac{4\Delta x^2}{P^2 r (r^2 - 1)} \left[ e^{P/4} \left( -\sinh \left( \frac{1}{4} P r \right) + r \cosh \left( \frac{1}{4} P r \right) \right) - r \right]$$

$$= \frac{4\Delta x^2}{P^2 (r^2 - 1)} \left[ e^{P/4} \left( -\frac{1}{4} P \sinh \left( \frac{1}{4} P r \right) + \cosh \left( \frac{1}{4} P r \right) \right) - 1 \right]. \tag{4.1.27}$$

Note that $I_2(-P;r) = I_1(P;r)$, therefore we define the following function

$$I(P;r) = \frac{4}{P^2 (r^2 - 1)} \left[ e^{-P/4} \left( -\frac{1}{4} P \sinh \left( \frac{1}{4} P r \right) + \cosh \left( \frac{1}{4} P r \right) \right) - 1 \right]. \tag{4.1.28}$$

Then, the integrals are given by $I_1(P;r) = \Delta x^2 I(P;r)$ and $I_2(P;r) = \Delta x^2 I(-P;r)$, and subsequently we find for the inhomogeneous flux

$$F_{j+1/2}^h = \Delta x \left( C(P;r) B(-Pr) I(P;r) s_j - C(-P;r) B(Pr) I(-P;r) s_{j+1} \right). \tag{4.1.29}$$

The expression \eqref{4.1.29} is also valid in case $Z = 0$, or equivalently $r = 0$, as will be shown in the next section.

4.1.3 Limiting cases

Several limiting cases can be investigated for scalar advection-diffusion-reaction complete flux scheme. The limiting cases should reduce to fluxes that can be found from their corresponding problems.

Advection-diffusion

In the case where reaction is negligible, i.e., $c = 0$, then $r = 1$ and the numerical fluxes reduce to

$$F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} \left( B(-P) \Phi_j - B(P) \Phi_{j+1} \right), \tag{4.1.30a}$$

$$F_{j+1/2}^v = W_1(P) \Delta x s_j - W_1(-P) \Delta x s_{j+1}. \tag{4.1.30b}$$

The scheme, with flux approximations presented by equations \eqref{4.1.30a}-\eqref{4.1.30b}, is known as the advection-diffusion weighted complete flux scheme (AD-WCF) as described in [6].
4.1. Scalar advection-diffusion-reaction scheme

Diffusion-reaction

In the case were advection is negligible, i.e., \( u = 0 \), then \( P = 0 \) and the numerical fluxes reduce to

\[
F_{j+1/2}^h = -\frac{\varepsilon}{\Delta x} \frac{\varphi_{j+1} - \varphi_j}{\sinh c \left( \frac{1}{4} \sqrt{D} \right)},
\]

(4.1.31a)

\[
F_{j+1/2}^i = \Delta x \frac{s_j - s_{j+1}}{8} \tanh c \left( \frac{1}{4} \sqrt{D} \right).
\]

(4.1.31b)

The scheme, with flux approximations presented by equations (4.1.31a)-(4.1.31b), is the scalar diffusion-reaction complete flux scheme presented in section 3.1.

Diffusion

In the case were both advection and reaction are negligible, i.e., \( u = c = 0 \), then

\[
F_{j+1/2}^h = -\frac{\varepsilon}{\Delta x} (\varphi_{j+1} - \varphi_j),
\]

(4.1.32a)

\[
F_{j+1/2}^i = \Delta x \frac{s_j - s_{j+1}}{8}.
\]

(4.1.32b)

The scheme, with flux approximations presented by equations (4.1.32a)-(4.1.32b), is the well-known standard central difference scheme with an additional inhomogeneous flux.

Degenerate eigenvalues

Degenerate eigenvalues of the characteristic equation for the BVP (4.1.6) are found when \( r = 0 \), corresponding to \( d = \frac{1}{4} \). The numerical fluxes in this case reduce to

\[
F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} C(P) \varphi_j - C(-P) \varphi_{j+1},
\]

(4.1.33a)

\[
F_{j+1/2}^i = \Delta x I(P) s_j - I(-P) s_{j+1},
\]

(4.1.33b)

where the functions \( C(P) \) and \( I(P) \) are defined by

\[
C(P) = e^{P/4} \left( \frac{P}{4} + 1 \right),
\]

(4.1.34a)

\[
I(P) = \frac{(P + 4) \left( 4e^{P/4} - P - 4 \right)}{4P^2}.
\]

(4.1.34b)

4.1.4 Scheme overview

Now, that expressions for the homogeneous and inhomogeneous fluxes have been found in sections 4.1.1 and 4.1.2, we can summarise the resulting schemes. To recap, the flux balance for the advection-diffusion-reaction type conservation law is given by (4.1.5), and reads

\[
F_{j+1/2} - F_{j-1/2} = \Delta x (c_j \varphi_j + s_j).
\]

(4.1.35)

For the advection-diffusion-reaction homogeneous flux (ADR-HF) scheme, we only use the homogeneous flux given by (4.1.12), i.e.,

\[
F_{j+1/2} = F_{j+1/2}^h,
\]

(4.1.36a)

\[
F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} (C(P; r) B(-Pr) \varphi_j - C(-P; r) B(Pr) \varphi_{j+1}),
\]

(4.1.36b)

\[
C(P; r) = e^{P(1-2r)/4} \left( \cosh \left( \frac{1}{4} Pr \right) + \frac{1}{4} P \sinh \left( \frac{1}{4} Pr \right) \right),
\]

(4.1.34b)
where \( r \in \mathbb{C} \). If additionally the inhomogeneous flux \([4.1.29]\) is taken into account, then the scheme is referred to as the advection-diffusion-reaction complete flux (ADR-CF) scheme, i.e.,
\[
F_{j+1/2}^h = F_{j+1/2}^h + F_{j+1/2}^i,
\]
\[
F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} (C(P; r)B(\varepsilon)\varphi_j - C(-P; r)B(\varepsilon)\varphi_{j+1}),
\]
\[
F_{j+1/2}^i = \Delta x (C(P; r)I(P; r)s_j - C(-P; r)B(\varepsilon)I(-P; r)s_{j+1}),
\]
with \( C(P; r) \) and \( I(P; r) \) defined by
\[
C(P; r) = e^{P(1 - 2r)/4} \left( \cosh \left( \frac{1}{4} Pr \right) + \frac{1}{4} P \sinh \left( \frac{1}{4} Pr \right) \right),
\]
\[
I(P; r) = \frac{4}{P^2 (r^2 - 1)} \left[ e^{-P/4} \left( \sinh \left( \frac{1}{4} Pr \right) + r \cosh \left( \frac{1}{4} Pr \right) \right) - r \right].
\]

These schemes can be compared with the advection-diffusion homogeneous flux and complete flux schemes, where the numerical flux is computed from a local BVP with source term \( \vec{s} = c \varphi + s \).

For the advection-diffusion homogeneous flux (AD-HF) scheme, the homogeneous flux reads [1, 2]
\[
F_{j+1/2} = \frac{\varepsilon}{\Delta x} (B(\varepsilon)\varphi_j - B(\varepsilon)\varphi_{j+1}),
\]
and for the advection-diffusion complete flux (AD-CF) scheme, the numerical fluxes [1, 2] read
\[
F_{j+1/2}^h = \frac{\varepsilon}{\Delta x} (B(\varepsilon)\varphi_j - B(\varepsilon)\varphi_{j+1}),
\]
\[
F_{j+1/2}^i = \Delta x \left( \frac{1}{2} - W(\varepsilon) \right) s_{u,j+1/2},
\]
where \( s_{u,j+1/2} \) is the upwind value of the source, i.e., \( s_{u,j+1/2} = s_j \) if \( u \geq 0 \) and \( s_{u,j+1/2} = s_{j+1} \) if \( u < 0 \).

### 4.2 System advection-diffusion-reaction scheme

In this section the finite volume method is applied to a system of one-dimensional conservation laws of advection-diffusion-reaction type. The following system is considered
\[
\frac{d}{dx} \left( U \varphi - \mathcal{E} \frac{d\varphi}{dx} \right) = C\varphi + s(\varphi),
\]
where \( U \) is the advection matrix, \( \mathcal{E} = (\varepsilon_{ij}) \) is the positive definite diffusion matrix and \( C\varphi + s(\varphi) \) represents the complete source, with \( C\varphi \) the linear part of the source. The system consists of \( m \) coupled ODE equations, i.e., \( \varphi \in \mathbb{R}^m, \mathcal{E} \in \mathbb{R}^{m \times m} \) etc. The flux vector \( f \) can be introduced such that
\[
f := U \varphi - \mathcal{E} \frac{d\varphi}{dx},
\]
\[
\frac{d}{dx} f = C\varphi + s(\varphi).
\]

Then, integrating equation [4.2.2b] over an interval \( I_j = [x_{j-1/2}, x_{j+1/2}] \) we obtain
\[
f(x_{j+1/2}) - f(x_{j-1/2}) = \int_{x_{j-1/2}}^{x_{j+1/2}} (C\varphi + s(\varphi)) \, dx.
\]
The numerical approximation of the flux \( f(x_{j+1/2}) \) will be denoted by \( F_{j+1/2} \) and the integral is approximated using the midpoint rule, resulting in

\[
F_{j+1/2} - F_{j-1/2} = \Delta x \left( C_j \varphi_j + s_j \right),
\]

(4.2.4)

where \( C_j := C(x_j) \), \( \varphi_j := \varphi(x_j) \) and \( s_j := s(\varphi_j) \). The numerical flux \( F_{j+1/2} \) is determined from the local BVP with constant advection matrix \( U \), diffusion matrix \( \mathcal{E} \) and reaction matrix \( C \), i.e.,

\[
\begin{align*}
\frac{d}{dx} \left( U \varphi - \mathcal{E} \frac{d\varphi}{dx} \right) &= C \varphi + s(\varphi), \quad x_j < x < x_{j+1}, \\
\varphi(x_j) &= \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1}.
\end{align*}
\]

(4.2.5a) (4.2.5b)

The numerical flux vector will consist of a homogeneous flux and an inhomogeneous flux, i.e., \( F_{j+1/2} = F_{jh} + F_{ji} \). First, we will derive the homogeneous flux \( F_{jh} \) followed by the derivation of the inhomogeneous flux \( F_{ji} \).

In the derivation of the system diffusion-reaction scheme in section 3.2, we introduced the matrix \( A_C := \mathcal{E}^{-1} C \) related to the Damköhler matrix and subsequently diagonalize the system using this matrix. Premultiplying the ODE system (4.2.5a) with the constant matrix \( \mathcal{E}^{-1} \) results in

\[
\frac{d}{dx} \left( \mathcal{E}^{-1} U \varphi - \frac{d\varphi}{dx} \right) = \mathcal{E}^{-1} C \varphi + \mathcal{E}^{-1} s(\varphi).
\]

(4.2.6)

Here, the matrices \( A_U = \mathcal{E}^{-1} U \) and \( A_C := \mathcal{E}^{-1} C \) are used to decouple an advection-diffusion system as in [1] or the diffusion-reaction system from section 3.2. In order to decouple the system (4.2.6), simultaneous diagonalization of both matrices is needed. However, this requires the matrices \( A_U \) and \( A_C \) to commute, which in general they do not:

\[
[A_U, A_C] = \mathcal{E}^{-1} U \mathcal{E}^{-1} C - \mathcal{E}^{-1} C \mathcal{E}^{-1} U.
\]

(4.2.7)

Even if \( U = u I \), as is the case for multicomponent diffusion, then relation (4.2.7) reduces to

\[
[A_U, A_C] = u \mathcal{E}^{-1} [\mathcal{E}^{-1}, C].
\]

(4.2.8)

In general, we cannot assume that \( \mathcal{E}^{-1} \) and \( C \) commute. Thus, we require another approach to solve this local ODE system. Just as in the derivation of the scalar inhomogeneous flux, we write the local ODE system as a first order system.

First, we introduce the (block) vector \( q = (\varphi, f)^T \in \mathbb{R}^{2m} \) such that the local system BVP 4.2.5 can be written as

\[
q' = Aq + b, \quad A = \begin{pmatrix} \mathcal{E}^{-1} U & -\mathcal{E}^{-1} C \\ C & 0 \end{pmatrix}, \quad b = \begin{pmatrix} 0 \\ s(\varphi) \end{pmatrix}.
\]

(4.2.9)

subject to the boundary conditions

\[
\begin{align*}
B_L q(x_j) + B_R q(x_{j+1}) &= \begin{pmatrix} \varphi_j \\ \varphi_{j+1} \end{pmatrix} := r, \\
B_L &= \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix}, \quad B_R = \begin{pmatrix} 0 & 0 \\ I & 0 \end{pmatrix}.
\end{align*}
\]

(4.2.10a) (4.2.10b)

In the above definitions of the block matrices \( B_L, B_R \), the matrices are partitioned into 4 equal-sized submatrices of size \( m \times m \). Furthermore, \( 0 \) denotes the zero matrix in expressions for a block matrix or a zero vector in the expression of the (block) vector \( b \). The rank of the block matrix \( A \) can be expressed as \( \text{rank}(A) = m + \text{rank}(C) \) and the eigenvalue problem for the block matrix \( A \) results in a quadratic eigenvalue problem (QEP) [23][24], see appendix B.1. These results will not be used in the derivation, however, they might provide some insight in the block matrix \( A \).
Next, the fundamental matrix \( Q \) is introduced such that
\[
Q' = AQ, \quad Q = \begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}. \tag{4.2.11}
\]
Therefore, the boundary conditions for \( Q \) are given by \( B_L Q(x_j) + B_R Q(x_{j+1}) = I \). In the above relation \( \Phi_1, \Phi_2, F_1, F_2 \) are fundamental matrix solutions. The fundamental matrices correspond to coefficients of the homogeneous solutions \( \varphi^h(x) \) and \( f^h(x) \), and are given by
\[
\varphi^h(x) = \Phi_1(x)\varphi_j + \Phi_2(x)\varphi_{j+1}, \tag{4.2.12a}
\]
\[
f^h(x) = F_1(x)\varphi_j + F_2(x)\varphi_{j+1}. \tag{4.2.12b}
\]
The fundamental matrix solutions \( \Phi_1(x) \) and \( \Phi_2(x) \) satisfy the homogeneous BVP \( 4.2.5 \), i.e. \( s(\varphi) = 0 \), with \( \Phi_1(x_j) = I, \Phi_2(x_{j+1}) = 0 \) and \( \Phi_1(x_j) = 0, \Phi_2(x_{j+1}) = I \), respectively.

Now, that the system BVP has been rewritten we can solve it. In section 4.2.1 we will solve the homogeneous ODE system and obtain the homogeneous flux. Next, the inhomogeneous flux is derived in section 4.2.2. Thereafter, the limiting cases of the scheme are investigated in section 4.2.3. Then, an overview of the resulting complete flux is given in section 4.2.4 and, finally, discrete mass and charge conservation is investigated in section 4.2.5.

### 4.2.1 Homogeneous flux

For the homogeneous flux \( F^h_{j+1/2} \) we only consider the homogeneous ODE system
\[
q' = Aq, \tag{4.2.13a}
\]
\[
B_L q(x_j) + B_R q(x_{j+1}) = r. \tag{4.2.13b}
\]
The general homogeneous solution to this ODE system is given by
\[
q^h(x) = e^{Ax}p, \tag{4.2.14}
\]
where \( p \) is a vector to be determined from the boundary conditions. Thus, applying the boundary conditions \( 4.2.13b \) results in
\[
B_L e^{Ax}p + B_R e^{Ax}p = r, \tag{4.2.15}
\]
which can be rewritten as
\[
(B_L + B_R e^{Ax}) e^{Ax}p = r. \tag{4.2.16}
\]
Let’s introduce the partitioning of the exponential matrix
\[
e^{Ax} = \begin{pmatrix} E_{11}(x) & E_{12}(x) \\ E_{21}(x) & E_{22}(x) \end{pmatrix}, \tag{4.2.17}
\]
where the submatrices are equally-sized. Note that \( e^{Ax} \) is regular, even if \( A \) is singular. Assuming that \( E_{12}(\Delta x) \) is regular, we can find the vector \( p \) from
\[
p = e^{-Ax} \begin{pmatrix} I & 0 \\ E_{11}(\Delta x) & E_{12}(\Delta x) \end{pmatrix}^{-1} r
= e^{-Ax} T^{-1} r, \tag{4.2.18}
\]
with
\[
T := \begin{pmatrix} I & 0 \\ E_{11}(\Delta x) & E_{12}(\Delta x) \end{pmatrix}. \tag{4.2.19}
\]
Substituting \( 4.2.18 \) in \( 4.2.14 \) results in the homogeneous solution \( q^h(x) \):
\[
q^h(x) = Q(x)r, \tag{4.2.20a}
\]
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with the fundamental matrix \( Q(x) \) given by

\[
Q(x) := e^{A(x-x_j)}T^{-1}.
\]  
(4.2.20b)

The inverse of \( T \) can be found directly by applying relation (B.1.2), i.e.,

\[
T^{-1} = \begin{pmatrix} I & 0 \\ - (E_{12}(\Delta x))^{-1}E_{11}(\Delta x) & (E_{12}(\Delta x))^{-1} \end{pmatrix}.
\]  
(4.2.21)

Then, the homogeneous flux \( f_{h}^{j+1/2} \) can be directly found from the second component of \( q_{h}^{j+1/2} \), i.e.,

\[
f_{h}^{j+1/2} = \left( E_{21}(\Delta x/2) - E_{22}(\Delta x/2) (E_{12}(\Delta x))^{-1} E_{11}(\Delta x) \right) \varphi_j \\
+ E_{22}(\Delta x/2) (E_{12}(\Delta x))^{-1} \varphi_{j+1}.
\]  
(4.2.22)

For the numerical flux we take \( F_{h}^{j+1/2} = f_{h}^{j+1/2} \).

In the derivation, we have assumed that \( E_{12}(\Delta x) \) is regular. Although, this is not proven in this thesis, the matrix is regular for the limiting cases investigated in section 4.2.3.

4.2.2 Inhomogeneous flux

In order to determine the inhomogeneous flux \( F_{i}^{j+1/2} \) we use the fundamental matrix solution \( Q(x) \), given by (4.2.20b), and apply variation of constants. Recall that the complete ODE system with boundary conditions is given by

\[
\frac{dq(x)}{dx} = Aq(x) + b(x),
\]  
(4.2.23a)

\[
B_L q(x_j) + B_R q(x_{j+1}) = r.
\]  
(4.2.23b)

Next, we apply variation of constants, i.e.

\[
q(x) = Q(x)\alpha(x),
\]  
(4.2.24)

therefore \( q' = Q'\alpha + Q\alpha' = AQ\alpha + b \) which implies \( \alpha'(x) = Q^{-1}(x)b(x) \), since \( Q' = AQ \). Upon integrating \( \alpha'(x) \) from \( x_j \) to \( x \) we find

\[
\alpha(x) - \alpha(x_j) = \int_{x_j}^{x} Q^{-1}(y)b(y)dy,
\]  
(4.2.25)

with \( \alpha(x_j) \) a constant vector. Applying the boundary conditions (4.2.23b) for \( q(x) \) results in

\[
B_L Q(x_j)\alpha(x_{j+1}) + B_R Q(x_{j+1})\left( \alpha(x_j) + \int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy \right) = r,
\]  
(4.2.26)

therefore

\[
\alpha(x_j) = r - B_R Q(x_{j+1})\int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy.
\]  
(4.2.27)

Substituting (4.2.25) and (4.2.27) in equation (4.2.24) we obtain the solution

\[
q(x) = Q(x)r - Q(x)B_R Q(x_{j+1})\int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy + Q(x)\int_{x_j}^{x} Q^{-1}(y)b(y)dy.
\]  
(4.2.28)
Applying the boundary conditions for $Q(x)$ this can be written as

\begin{align}
  q(x) &= q^h(x) + q^l(x), \\
  q^h(x) &:= Q(x)r, \\
  q^l(x) &:= \int_{x_j}^{x_{j+1}} G(x; y)b(y)dy
\end{align}

with Green’s function $G(x; y)$ defined by

\[
  G(x; y) = \begin{cases} 
    Q(x)B_L Q(x_j)Q^{-1}(y) & \text{for } x_j \leq y \leq x, \\
    -Q(x)B_R Q(x_{j+1})Q^{-1}(y) & \text{for } x < y \leq x_{j+1}.
  \end{cases}
\]

Note that (4.2.29) defines the complete solution, i.e., $\varphi(x)$ and $f(x)$ on the entire interval $[x_j, x_{j+1}]$. We are only interested in the inhomogeneous flux at the interface $x = x_{j+1/2}$, therefore the inhomogeneous solution at the interface is given by

\[
  q_{j+1/2} = \int_{x_j}^{x_{j+1/2}} G(x_{j+1/2}; y)b(y)dy
\]

\[
  = \int_{x_j}^{x_{j+1/2}} Q(x_{j+1/2})B_L Q(x)Te^{-A(y-x_j)}b(y)dy \\
  - \int_{x_{j+1/2}}^{x_{j+1}} Q(x_{j+1})B_R Q(x_{j+1})Te^{-A(y-x_j)}b(y)dy.
\]

The integrals can be evaluated if we assume that the source $b(x)$ is constant within the control volume $x_{j-1/2} < x < x_{j+1/2}$, i.e.,

\[
b(x) = \begin{cases} 
    b_j, & \text{for } x_{j-1/2} < x < x_{j+1/2}, \\
    b_{j+1}, & \text{for } x_{j+1/2} < x < x_{j+3/2}.
  \end{cases}
\]

Next, we introduce the auxiliary variables for the integrals

\[
  Z_1 := \int_{x_j}^{x_{j+1/2}} e^{-A(y-x_j)}dy, \\
  Z_2 := \int_{x_{j+1/2}}^{x_{j+1}} e^{-A(y-x_j)}dy.
\]

Note, that the second integral is simply the first integral with the interval displaced by $\Delta x/2$. Therefore, $Z_2 = \exp(-A\Delta x/2)Z_1$. The integral $Z_1$ needs to be carefully evaluated, since $A$ is singular if the reaction matrix $C$ is singular, see appendix B.1. Next, we assume that the matrix $A$ can be spectrally decomposed such that

\[
  A = V\Lambda V^{-1}, \quad \Lambda := \text{diag}(\lambda_1, ..., \lambda_{2m}), \quad V := (v_1, ..., v_{2m}),
\]

for the corresponding eigenvalue problem

\[
  (A - \lambda_k I)v_k = 0.
\]

Then, the integral can be evaluated as follows

\[
  \int_{x_j}^{x_{j+1/2}} e^{-A(y-x_j)}dy = V \int_{x_j}^{x_{j+1/2}} e^{-\Lambda(y-x_j)}dyV^{-1},
\]

\[
  \int_{x_j}^{x_{j+1}} e^{-A(y-x_j)}dy = \text{diag} \left( \int_{x_j}^{x_{j+1}} e^{-\lambda_m(y-x_j)}dy \right).
\]
Note that if the matrix \( A \) is singular, one of its eigenvalues \( \lambda_m = 0 \). Taking this into account, the resulting integral is given by

\[
\int_{x_j}^{x_{j+1/2}} e^{-\lambda_m(y-x)} \, dy = -\frac{1}{\lambda_m} \left( e^{-\lambda_m \Delta x/2} - 1 \right) = \frac{\Delta x}{2} \left( B \left( -\frac{1}{2} \lambda_m \Delta x \right) \right)^{-1}.
\] (4.2.36)

Here \( B(z) \) is the Bernoulli function as defined by equation (4.1.9). Note that \( B(A) \) will be regular, even if the matrix \( A \) is singular. Applying the assumption (4.2.31) and substituting (4.2.35a)-(4.2.35b) and (4.2.36) in (4.2.30) results in

\[
q_{j+1/2} = Q(x_{j+1/2}) B_l Q(x_j) T \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} \frac{\Delta x}{2} b_j
\]
\[
- Q(x_{j+1/2}) B_l Q(x_{j+1}) T \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} e^{-A \Delta x/2} \frac{\Delta x}{2} b_{j+1}.
\] (4.2.37)

Using the definition of the fundamental matrix \( Q \), from equation (4.2.11), and the definition of \( T \), from equation (4.2.19), then the numerical inhomogeneous flux reads

\[
F_{j+1/2} = \frac{\Delta x}{2} \left( F_1(x_{j+1/2}) I_1 s_j - F_2(x_{j+1/2}) I_2 s_{j+1} \right),
\] (4.2.38a)

with

\[
I_1 := \left[ \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} \right]_{12},
\] (4.2.38b)

\[
I_2 := \left[ \left( B \left( \frac{1}{2} A \Delta x \right) \right)^{-1} \right]_{12}.
\] (4.2.38c)

In the expressions of \( I_i \) we take the \( 12 \) block, i.e. the \( m \times m \) top right block of the matrix within the brackets. In the above relation for \( I_2 \) the term was simplified. The original expression for \( I_2 \) is given by

\[
I_2 = E_{11}(\Delta x) \left[ \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} e^{-A \Delta x/2} \right]_{12}
\]
\[
+ E_{12}(\Delta x) \left[ \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} e^{-A \Delta x/2} \right]_{22}.
\] (4.2.39)

However, the term can be simplified by using the spectral decomposition of \( A \), and the relation \( \exp(z)/B(-z) = 1/B(z) \) and noting that

\[
e^{A \Delta x} \left( B \left( -\frac{1}{2} A \Delta x \right) \right)^{-1} e^{-A \Delta x/2} = \left( \begin{array}{c} 1 \\ \vdots \\ I_2 \end{array} \right).
\] (4.2.40)

### 4.2.3 Limiting cases

Several limiting cases can be investigated for this scheme. The matrix \( A \) can in these cases be reduced to a simpler form and we can find the matrix exponential analytically. To recap, the system matrix \( A \) is given by

\[
A = \begin{pmatrix} \mathcal{E}^{-1} U & -\mathcal{E}^{-1} \\ C & 0 \end{pmatrix},
\] (4.2.41)

and the matrix exponential of \( A \) can be found from

\[
\exp (A) = \sum_{k=0}^{\infty} \frac{1}{k!} A^k.
\] (4.2.42)
Advection-diffusion

In the case were reaction is negligible, i.e., $C = 0$, the matrix $A$ reduces to

$$ A = \begin{pmatrix} E^{-1}U & -E^{-1} \\ 0 & 0 \end{pmatrix}. $$

(4.2.43)

Using the definition of the Péclet matrix $P = E^{-1}U\Delta x$, the matrix power of $A\Delta x$ with $k > 0$ is given by

$$(A\Delta x)^k = \begin{pmatrix} (P)^k & -(P)^{k-1}E^{-1}\Delta x \\ 0 & 0 \end{pmatrix}.$$  

(4.2.44)

The matrix exponential of $A\Delta x$ can then be expressed as

$$ \exp(A\Delta x) = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} + \sum_{k=1}^{\infty} \frac{1}{k!} \begin{pmatrix} (P)^k & -(P)^{k-1}E^{-1}\Delta x \\ 0 & 0 \end{pmatrix}. $$

(4.2.45)

The Péclet matrix can be singular in case the advection matrix $U$ is singular, therefore we introduce the spectral decomposition of the Péclet matrix given by $P = V\Lambda V^{-1}$ with $V = (v_1, ..., v_m)$ and $\Lambda = \text{diag}(\lambda_1, ..., \lambda_m)$. The top right block of the matrix exponential is now given by

$$ -\sum_{k=1}^{\infty} \frac{1}{k!} (P)^{k-1}E^{-1}\Delta x = -V \sum_{k=1}^{\infty} \frac{1}{k!} (A)^{k-1}V^{-1}E^{-1}\Delta x $$

$$ = -V \text{diag} \left( \sum_{k=1}^{\infty} \frac{1}{k!} \lambda_m^{k-1} \right) V^{-1}E^{-1}\Delta x. $$

(4.2.46)

The series in (4.2.46) can be expressed as

$$ \sum_{k=1}^{\infty} \frac{1}{k!} \lambda_m^{k-1} = \frac{1}{\lambda_m} \left( \sum_{k=0}^{\infty} \frac{1}{k!} \lambda_m^k - 1 \right) = \frac{\exp(\lambda_m) - 1}{\lambda_m} = (B(\lambda_m))^{-1}. $$

(4.2.47)

Using equations (4.2.46)-(4.2.47) the matrix exponential can be written as

$$ \exp(A\Delta x) = \begin{pmatrix} \exp(P) & -(B(P))^{-1}E^{-1}\Delta x \\ 0 & I \end{pmatrix}. $$

(4.2.48)

Substituting (4.2.48) in the homogeneous flux (4.2.22), we find

$$ f_{j+1/2}^h = \frac{1}{\Delta x} E B(P) \left[ \exp(P) \varphi_j - \varphi_{j+1} \right] $$

$$ = \frac{1}{\Delta x} E \left( B(-P) \varphi_j - B(P) \varphi_{j+1} \right). $$

(4.2.49)

This is the expected system advection-diffusion homogeneous flux.

For the expression of the inhomogeneous flux (4.2.38a) we require the inverse of the Bernoulli function, therefore, we once again use the spectral decomposition of $P$ and relation (4.2.47) resulting in

$$ \left( B \left( \pm \frac{1}{2} A\Delta x \right) \right)^{-1} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} + \sum_{k=2}^{\infty} \frac{1}{k!} \begin{pmatrix} (\pm \frac{1}{2} P)^{k-2}E^{-1}\Delta x & \pm \frac{1}{2} (\pm \frac{1}{2} P)^{k-1}E^{-1}\Delta x \\ 0 & 0 \end{pmatrix} $$

$$ = \left( B \left( \pm \frac{1}{2} P \right) \right)^{-1} + \frac{1}{2} W_2 \left( \pm \frac{1}{2} P \right) E^{-1}\Delta x. $$

(4.2.50)
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Here, we have defined $W_2(z)$ as the result of the series:

$$
\sum_{k=2}^{\infty} \frac{1}{k!} z^{k-2} = \frac{\exp(z) - z - 1}{z^2} =: W_2(z),
$$

(4.2.51)

with $W_2(0) = \frac{1}{2}$. In the expression of the inhomogeneous flux (4.2.38a), the following term has to be considered for the eigenvalues of the Péclet matrix:

$$
B(z) W_2 \left( \frac{1}{2} z \right) = 4 \frac{\exp(z/2) - z/2 - 1}{z(\exp(z) - 1)} = 4 W_1(-z),
$$

(4.2.52)

where $W_1(z)$ is defined in (4.1.11). Substituting (4.2.50) in (4.2.38a), and using the spectral decomposition of the Péclet matrix and applying relation (4.2.52), we obtain

$$
F_{j+1/2}^i = \left( \frac{\Delta x}{2} \right)^2 \left( F_1 (x_{j+1/2}) W_2 \left( -\frac{1}{2} \hat{P} \right) \mathcal{E}^{-1} s_j + F_2 (x_{j+1/2}) W_2 \left( \frac{1}{2} \hat{P} \right) \mathcal{E}^{-1} s_{j+1} \right)
$$

$$
= \frac{\Delta x}{4} \mathcal{E} \left( B(-\hat{P}) W_2 \left( -\frac{1}{2} \hat{P} \right) \mathcal{E}^{-1} s_j - B(\hat{P}) W_2 \left( \frac{1}{2} \hat{P} \right) \mathcal{E}^{-1} s_{j+1} \right)
$$

$$
= \Delta x \mathcal{E} \left( W_1(\hat{P}) \mathcal{E}^{-1} s_j - W_1(-\hat{P}) \mathcal{E}^{-1} s_{j+1} \right)
$$

$$
= \Delta x \left( W_1(\hat{P}) s_j - W_1(-\hat{P}) s_{j+1} \right),
$$

(4.2.53)

where $\hat{P} := \mathcal{E} P \mathcal{E}^{-1}$. This inhomogeneous flux appears in the system advection-diffusion weighted complete flux (AD-WCF) scheme described in [6].

**Diffusion-reaction**

In the case were advection is negligible, i.e., $U = 0$, the matrix $A$ reduces to

$$
A = \begin{pmatrix} 0 & -\mathcal{E}^{-1} \\ C & 0 \end{pmatrix}.
$$

(4.2.54)

Next, we need the definition of the Damköhler matrix $D = \mathcal{E}^{-1} C (\Delta x)^2$ and its auxiliary matrix $\hat{D}$, for which $\hat{D}^2 = -D$ holds. Then, the matrix power of $A \Delta x$ with $k \geq 0$ is given by

$$
(A \Delta x)^{2k} = \begin{pmatrix} \hat{D}^{2k} & 0 \\ 0 & \mathcal{E} \hat{D}^{2k} \mathcal{E}^{-1} \end{pmatrix},
$$

(4.2.55a)

$$
(A \Delta x)^{2k+1} = \begin{pmatrix} 0 & -\mathcal{E} \hat{D}^{2k+2} \mathcal{E}^{-1} \Delta x \\ -\frac{1}{\Delta x} \mathcal{E} \hat{D}^{2k+2} \mathcal{E}^{-1} \Delta x & 0 \end{pmatrix}.
$$

(4.2.55b)

The matrix exponential of $A \Delta x$ can then be expressed as

$$
\exp(A \Delta x) = \begin{pmatrix} \cosh(\hat{D}) & -\sinh(\hat{D}) \mathcal{E}^{-1} \Delta x \\ -\frac{1}{\Delta x} \mathcal{E} \hat{D} \sinh(\hat{D}) & \mathcal{E} \cosh(\hat{D}) \mathcal{E}^{-1} \end{pmatrix},
$$

(4.2.56)

where the following series have been applied

$$
cosh(z) = \sum_{k=0}^{\infty} \frac{1}{(2k)!} z^{2k},
$$

(4.2.57a)

$$
\sinh(z) = \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} z^{2k+1}.
$$

(4.2.57b)
Substituting (4.2.56) in the homogeneous flux (4.2.22), we find

\[
\begin{align*}
    f_{j+1/2}^h &= -\frac{1}{\Delta x} E \left[ \cosh \left( \frac{1}{2} \hat{D} \right) \left( \sinh \left( \hat{D} \right) \right)^{-1} \left( \varphi_{j+1} - \cosh \left( \hat{D} \right) \varphi_j \right) \right] \\
    &= -\frac{1}{\Delta x} E \left( \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} \left( \varphi_{j+1} - \varphi_j \right),
\end{align*}
\]

where we have used the following identities

\[
\cosh(2z) = 2 \sinh(z)^2 + 1, \\
\sinh(2z) = 2 \sinh(z) \cosh(z).
\]

This is the expected diffusion-reaction homogeneous flux from section 3.2.1, cf. (3.2.42).

For the expression of the inhomogeneous flux (4.2.38a) we require the inverse of the Bernoulli function, therefore, we use the spectral decomposition of the Damköhler matrix \( D \) and relation (4.2.47) resulting in

\[
\left( B \left( \pm \frac{1}{2} A \Delta x \right) \right)^{-1} = \left( \begin{array}{cc} I & 0 \\ 0 & I \end{array} \right) + \sum_{k=1}^{\infty} \frac{1}{(2k+1)!} \left( \begin{array}{cc} \left( \frac{1}{2} \hat{D} \right)^{2k} & 0 \\ 0 & E \left( \frac{1}{2} \hat{D} \right)^{2k} \epsilon^{-1} \end{array} \right) \\
+ \sum_{k=1}^{\infty} \frac{1}{(2k)!} \left( \begin{array}{cc} 0 & \mp \frac{1}{2} \left( \frac{1}{2} \hat{D} \right)^{2k-2} \epsilon^{-1} \Delta x \\ \mp \frac{2}{\Delta x} E \left( \cosh \left( \frac{1}{2} \hat{D} \right) - I \right) & E \sinh \left( \frac{1}{2} \hat{D} \right) \epsilon^{-1} \end{array} \right)
\]

Here, we have defined \( W_3(z) \) as the result of the series:

\[
\sum_{k=1}^{\infty} \frac{1}{(2k)!} z^{2k-2} = \frac{\cosh(z) - 1}{z^2} = W_3(z),
\]

with \( W_3(0) = \frac{1}{2} \). The product of \( 1/\sinh(z) \) and \( W_3(z) \) is given by

\[
\frac{W_3(z)}{\sinh(z)} = \frac{\cosh(z) - 1}{z \sinh(z)} = \frac{1}{2} \tanh \left( \frac{1}{2} z \right).
\]

Substituting (4.2.59) in (4.2.38a), and using the spectral decomposition of the Damköhler matrix and applying relation (4.2.61), we obtain

\[
\begin{align*}
    F_{j+1/2}^i &= \left( \frac{\Delta x}{2} \right)^2 \left( F_1 (x_{j+1/2}) W_3 \left( \frac{1}{2} \hat{D} \right) \epsilon^{-1} s_j + F_2 (x_{j+1/2}) W_3 \left( \frac{1}{2} \hat{D} \right) \epsilon^{-1} s_{j+1} \right) \\
    &= \frac{\Delta x}{4} E \left( \sinh \left( \frac{1}{2} \hat{D} \right) \right)^{-1} W_3 \left( \frac{1}{2} \hat{D} \right) \epsilon^{-1} (s_j - s_{j+1}) \\
    &= \frac{\Delta x}{8} E \tanh \left( \frac{1}{4} \hat{D} \right) \epsilon^{-1} (s_j - s_{j+1}).
\end{align*}
\]

This is the expected diffusion-reaction inhomogeneous flux from section 3.2.2, cf. (3.2.65).
4.2. System advection-diffusion-reaction scheme

Diffusion

In the case were both advection and reaction are negligible, i.e., \( U = C = 0 \), the matrix \( A \) reduces to
\[
A = \begin{pmatrix} 0 & -E^{-1} \\ 0 & 0 \end{pmatrix}.
\] (4.2.63)
The matrix exponential of \( A\Delta x \) can directly be found, since \( A^2 = 0 \), i.e.,
\[
\exp (A\Delta x) = I + A\Delta x = \begin{pmatrix} I & -E^{-1}\Delta x \\ 0 & I \end{pmatrix}.
\] (4.2.64)
Substituting (4.2.64) in the homogeneous flux (4.2.22), we find
\[
f_{h,j+1/2} = -\frac{1}{\Delta x} E \left( \varphi_{j+1} - \varphi_j \right).
\] (4.2.65)
This is the expected system central difference homogeneous flux, cf. (3.2.43).

The inverse of the Bernoulli function for \( \pm \frac{1}{2} A\Delta x \), can also be quickly found, i.e.,
\[
\left( B \left( \pm \frac{1}{2} A\Delta x \right) \right)^{-1} = \pm \frac{1}{4} A\Delta x + I = \begin{pmatrix} I & \mp \frac{1}{4} E^{-1}\Delta x \\ 0 & I \end{pmatrix}.
\] (4.2.66)
Substituting (4.2.66) in (4.2.38a), we obtain
\[
F_{i,j+1/2} = \frac{\Delta x}{2} \left( \begin{pmatrix} 1 \\ \frac{1}{4} E^{-1}\Delta x \end{pmatrix} s_j - \frac{1}{\Delta x} \frac{1}{4} E^{-1}\Delta x s_{j+1} \right)
= \frac{\Delta x}{8} (s_j - s_{j+1}).
\] (4.2.67)
This is the expected system inhomogeneous flux, cf. (3.2.66).

4.2.4 Scheme overview

Now, that expressions for the homogeneous and inhomogeneous flux vectors have been found in sections 4.2.1 and 4.2.2, we can summarise the resulting schemes. To recap, the flux balance for the system advection-diffusion-reaction type conservation law is given by (4.2.4), and reads
\[
F_{j+1/2} - F_{j-1/2} = \Delta x \left( C_j \varphi_j + s_j \right).
\] (4.2.68)
For the advection-diffusion-reaction homogeneous flux (ADR-HF) scheme, we only use the homogeneous flux given by (4.2.22), i.e., \( F_{j+1/2} = F_{h,j+1/2} \). If additionally the inhomogeneous flux (4.2.38a) is taken into account, then the scheme is referred to as the advection-diffusion-reaction complete flux (ADR-CF) scheme, i.e., \( F_{j+1/2} = F_{h,j+1/2} + F_{i,j+1/2} \).

These schemes can be compared with the system advection-diffusion homogeneous flux and complete flux schemes, where the numerical flux vector is computed from a local BVP with source term \( \tilde{s} = C\varphi + s \). For the advection-diffusion homogeneous flux (AD-HF) scheme, the homogeneous flux reads [1]
\[
F_{h,j+1/2} = \frac{1}{\Delta x} E \left( B(-P)\varphi_j - B(P)\varphi_{j+1} \right).
\] (4.2.69a)
For the advection-diffusion complete flux (AD-CF) scheme, the numerical fluxes [1] read
\[
F_{j+1/2} = F_{h,j+1/2} + F_{i,j+1/2}, \quad (4.2.70a)
F_{h,j+1/2} = \frac{1}{\Delta x} E \left( B(-P)\varphi_j - B(P)\varphi_{j+1} \right), \quad (4.2.70b)
F_{i,j+1/2} = \Delta x \left( \frac{1}{2} I - W(\hat{P}) \right) s_{n,j+1/2}, \quad (4.2.70c)
where $\hat{P} = \mathbf{EPE}^{-1}$ and $s_{n,j+1/2}$ is the upwind value for the source term given by

$$s_{n,j+1/2} = \frac{1}{2} (I + \sigma) s_j + \frac{1}{2} (I - \sigma) s_{j+1}, \quad \sigma = \text{sgn} \left( \hat{P} \right).$$

### 4.2.5 Discrete mass and charge conservation

In a general multicomponent mixture consisting of $m$ species where mass and charge should be conserved, the vectors $\mathbf{1}^T$ and $\mathbf{r}^T$ should be left-eigenvectors of the discretisation coefficient matrices [17] that appear in the numerical flux vector $F_{j+1/2}$. The vectors $\mathbf{1} = (1, ..., 1)^T$ and $\mathbf{r} = (q_1/m_1, ..., q_m/m_m)^T$ are defined in section 2.4. In order to prove discrete mass and charge conservation, the advection, diffusion and reaction matrices should have $\mathbf{1}^T$ and $\mathbf{r}^T$ as left-eigenvectors. For the diffusion and reaction matrices it was already noted that the matrices have $\mathbf{1}^T$ and $\mathbf{r}^T$ as left eigenvectors, see section 3.2.4. For the advection matrix it simply follows since the advection matrix is a scalar matrix, i.e., $\mathbf{U} = u \mathbf{I}$.

For the advection matrix the eigenvalues for both eigenvectors $\mathbf{1}^T$ and $\mathbf{r}^T$ are given by $u$, while for the reaction matrix both eigenvectors have the eigenvalue 0. For the diffusion matrix we will denote the corresponding eigenvalues by

$$(4.2.72a) \quad 1^T \mathbf{E} = \varepsilon^m \mathbf{1}^T,$$

$$(4.2.72b) \quad r^T \mathbf{E} = \varepsilon^c r^T,$$

with the values given by

$$\varepsilon^m := \beta \sigma^m,$$

$$\varepsilon^c := \gamma r^T \rho_c.$$  

The one-dimensional steady-state advection-diffusion-reaction mass conservation law is given by

$$\frac{d}{dx} \left( U y - \mathbf{E} \frac{dy}{dx} \right) = C y + s(y),$$

with $C y = \text{diag}(m) \omega$ the linear part of the reaction source term. The advection-diffusion-reaction complete flux discretized scheme is given by

$$- \alpha_{j-1/2} y_{j-1} + \left( \alpha_{j+1/2} + \beta_{j-1/2} \right) y_j - \beta_{j+1/2} y_{j+1} = \Delta x \left( C_j y_j + \gamma_{j-1/2} s_{j-1} + \left( I - \gamma_{j+1/2} + \delta_{j-1/2} \right) s_j - \delta_{j+1/2} s_{j+1} \right),$$

with the coefficient matrices $\alpha_{j+1/2}, \beta_{j+1/2}$ etc. defined by

$$\alpha_{j+1/2} := E_{21}(\Delta x/2) - E_{22}(\Delta x/2) (E_{12}(\Delta x))^{-1} E_{11}(\Delta x),$$

$$\beta_{j+1/2} := -E_{22}(\Delta x/2) (E_{12}(\Delta x))^{-1},$$

$$\gamma_{j+1/2} := \frac{1}{2} F_1(x_{j+1/2}) I_1,$$

$$\delta_{j+1/2} := -\frac{1}{2} F_2(x_{j+1/2}) I_2.$$  

The fluxes for this scheme are described by a complicated structure of advection, diffusion and reaction matrices. Therefore, we first introduce the dimensionless matrix $\mathbf{A}$ such that

$$A \Delta x = \left( \begin{array}{cc} I & 0 \\ 0 & \frac{1}{\Delta x} \mathbf{E} \end{array} \right) A \left( \begin{array}{cc} I & 0 \\ 0 & \Delta x \mathbf{E}^{-1} \end{array} \right).$$

(4.2.76)
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with

\[
\mathcal{A} = \begin{pmatrix} P & -I \\ D & 0 \end{pmatrix}.
\] (4.2.77)

Note that this is equivalent to scaling the fluxes with \( E^{-1} \Delta x \) in order to make them dimensionless. The matrix exponential of \( \mathcal{A} \Delta x \) can now be expressed as

\[
\exp(\mathcal{A} \Delta x) = \begin{pmatrix} I & 0 \\ 0 & \frac{1}{\Delta x} E \end{pmatrix} \exp(\mathcal{A}) \begin{pmatrix} I & 0 \\ 0 & \Delta x E^{-1} \end{pmatrix}.
\] (4.2.78)

Furthermore, the matrix exponential of \( \mathcal{A} \) can be found from

\[
\exp(\mathcal{A}) = \sum_{k=0}^{\infty} \frac{1}{k!} \mathcal{A}^k.
\] (4.2.79)

Now, we can exploit the structure of the block matrix \( \mathcal{A} \) to find that

\[
\mathcal{A}^k = \begin{pmatrix} \mathcal{P}^k_{11}(P, D) & \mathcal{P}^k_{12}(P, D) \\ \mathcal{P}^k_{21}(P, D) & \mathcal{P}^k_{22}(P, D) \end{pmatrix},
\] (4.2.80)

with \( \mathcal{P}^k_{ij}(P, D) \) multivariate polynomials of, in general, non-commuting matrices and a polynomial degree of at most \( k \). A recurrence relation for the polynomials can be found using \( \mathcal{A}^{k+1} = \mathcal{A} \mathcal{A}^k \), resulting in

\[
\mathcal{P}^{k+1}_{11}(P, D) = P \mathcal{P}^k_{11}(P, D) - \mathcal{P}^k_{21}(P, D),
\] (4.2.81a)

\[
\mathcal{P}^{k+1}_{12}(P, D) = P \mathcal{P}^k_{12}(P, D) - \mathcal{P}^k_{22}(P, D),
\] (4.2.81b)

\[
\mathcal{P}^{k+1}_{21}(P, D) = D \mathcal{P}^k_{11}(P, D),
\] (4.2.81c)

\[
\mathcal{P}^{k+1}_{22}(P, D) = D \mathcal{P}^k_{12}(P, D).
\] (4.2.81d)

Upon substituting relations (4.2.81a)-(4.2.81d) in (4.2.81a)-(4.2.81d) we find for \( k \geq 1 \)

\[
\mathcal{P}^{k+1}_{11}(P, D) = P \mathcal{P}^k_{11}(P, D) - \mathcal{P}^k_{21}(P, D),
\] (4.2.82a)

\[
\mathcal{P}^{k+1}_{12}(P, D) = P \mathcal{P}^k_{12}(P, D) - \mathcal{P}^k_{22}(P, D),
\] (4.2.82b)

with initial conditions

\[
\begin{pmatrix} \mathcal{P}^0_{11} & \mathcal{P}^0_{12} \\ \mathcal{P}^0_{21} & \mathcal{P}^0_{22} \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}, \quad \begin{pmatrix} \mathcal{P}^0_{11} & \mathcal{P}^0_{12} \\ \mathcal{P}^0_{21} & \mathcal{P}^0_{22} \end{pmatrix} = \begin{pmatrix} P & -I \\ D & 0 \end{pmatrix}.
\] (4.2.83)

Note that the recurrence relations (4.2.82a)-(4.2.82b) only differ in initial conditions and due to this particular set of initial conditions, i.e., \( \mathcal{P}^0_{11} = -I = -\mathcal{P}^0_{11} \) and \( \mathcal{P}^0_{12} = -P = -\mathcal{P}^0_{12} \), the following relation holds

\[
\mathcal{P}^{k+1}_{12}(P, D) = -\mathcal{P}^k_{11}(P, D).
\] (4.2.84)

Finally, the recurrence relations (4.2.81a)-(4.2.81d) can be written as

\[
\mathcal{P}^{k+1}_{11}(P, D) = P \mathcal{P}^k_{11}(P, D) - \mathcal{P}^k_{21}(P, D),
\] (4.2.85a)

\[
\mathcal{P}^{k+1}_{12}(P, D) = -\mathcal{P}^k_{11}(P, D),
\] (4.2.85b)

\[
\mathcal{P}^{k+1}_{21}(P, D) = D \mathcal{P}^k_{11}(P, D),
\] (4.2.85c)

\[
\mathcal{P}^{k+1}_{22}(P, D) = -D \mathcal{P}^k_{11}(P, D).
\] (4.2.85d)

The first six polynomials of \( \mathcal{P}^k_{11}(P, D) \) are presented in table 4.1.
Table 4.1: First six multivariate polynomials \( P^k_{ij}(P,D) \) of, in general, non-commuting matrices \( P \) and \( D \).

| \( P^0_{11}(P,D) \) | \( I \) |
| \( P^1_{11}(P,D) \) | \( P \) |
| \( P^2_{11}(P,D) \) | \( P^2 - D \) |
| \( P^3_{11}(P,D) \) | \( P^3 - PD - DP \) |
| \( P^4_{11}(P,D) \) | \( P^4 - P^2 D - PDP - DP^2 + D^2 \) |
| \( P^5_{11}(P,D) \) | \( P^5 - P^3 D - P^2 DP - PDP^2 + PD^2 - DP^3 + DPD + D^2 P \) |

In order to determine if there is discrete mass and charge conservation, we premultiply the recurrence relations for \( P^k_{ij}(P,D) \) by their respective left eigenvectors. Solving the resulting scalar recurrence relation results in the following eigenvalues for the polynomials with \( k \geq 1 \),

\[
1^T P^k_{11}(P,D) = (p^m)^k 1^T, \quad r^T P^k_{11}(P,D) = (p^c)^k r^T, \quad (4.2.86a)
\]
\[
1^T P^k_{12}(P,D) = -(p^m)^k 1^T, \quad r^T P^k_{12}(P,D) = -(p^c)^k r^T, \quad (4.2.86b)
\]
\[
1^T P^k_{21}(P,D) = 0^T, \quad r^T P^k_{21}(P,D) = 0^T, \quad (4.2.86c)
\]
\[
1^T P^k_{22}(P,D) = 0^T, \quad r^T P^k_{22}(P,D) = 0^T. \quad (4.2.86d)
\]

Here, \( p^m := \Delta x u / \varepsilon m \) and \( p^c := \Delta x u / \varepsilon c \) denote the Péclet numbers for the \( \sigma^m \) and \( \sigma^c \) species, respectively. The blocks of \( \exp(A \Delta x \sigma) \) can be found from equations \((4.2.78)-(4.2.79)\), where \( \sigma(x) = (x - x_j) / \Delta x \) is the scaled coordinate, resulting in the series

\[
\exp(A \Delta x \sigma) = \sum_{k=0}^{\infty} \frac{1}{k!} \left( \frac{\p^k_{11}(\sigma P, \sigma D)}{\Delta x} \right) \Delta x \p^k_{12}(\sigma P, \sigma D) \p^k_{21}(\sigma P, \sigma D) \p^k_{22}(\sigma P, \sigma D) \varepsilon^{-1} \quad (4.2.87)
\]

The submatrices \( E_{ij}(\Delta x \sigma) \) then have the following eigenvalues

\[
1^T E_{11}(\Delta x \sigma) = \exp(p^m \sigma) 1^T, \quad r^T E_{11}(\Delta x \sigma) = \exp(p^c \sigma) r^T, \quad (4.2.88a)
\]
\[
1^T E_{12}(\Delta x \sigma) = - \frac{\exp(p^m \sigma) - 1}{p^m \sigma} \Delta x 1^T, \quad r^T E_{12}(\Delta x \sigma) = - \frac{\exp(p^c \sigma) - 1}{p^c \sigma} \Delta x r^T, \quad (4.2.88b)
\]
\[
1^T E_{21}(\Delta x \sigma) = 0^T, \quad r^T E_{21}(\Delta x \sigma) = 0^T, \quad (4.2.88c)
\]
\[
1^T E_{22}(\Delta x \sigma) = 1^T, \quad r^T E_{22}(\Delta x \sigma) = r^T. \quad (4.2.88d)
\]

Similarly, the eigenvalues of the matrices \( I_1, I_2 \) can be derived from their respective series:

\[
I_1 = -\frac{1}{2} \sum_{k=2}^{\infty} \frac{1}{k!} \p^k_{12} \left( -\frac{1}{2} P, -\frac{1}{2} D \right) \Delta x \varepsilon^{-1}, \quad (4.2.89a)
\]
\[
I_2 = \frac{1}{2} \sum_{k=2}^{\infty} \frac{1}{k!} \p^k_{12} \left( \frac{1}{2} P, \frac{1}{2} D \right) \Delta x \varepsilon^{-1}. \quad (4.2.89b)
\]

Therefore, the following eigenvalues for the coefficient matrices \( \alpha_{j+1/2}, \beta_{j+1/2} \) etc., can be derived
from the eigenvalues \((4.2.88)\). The result for mass conservation reads

\[
1^T \alpha_{j+1/2} = \frac{p_{j+1/2}^m}{\exp(p_{j+1/2})} \epsilon_{j+1/2} \exp(p_{j+1/2}) 1^T = \frac{\epsilon_{j+1/2}}{\Delta x} B(p_{j+1/2}) 1^T, \tag{4.2.90a}
\]

\[
1^T \beta_{j+1/2} = \frac{p_{j+1/2}^c}{\exp(p_{j+1/2})} \epsilon_{j+1/2} 1^T = \frac{\epsilon_{j+1/2}}{\Delta x} B(p_{j+1/2}) 1^T, \tag{4.2.90b}
\]

\[
1^T \gamma_{j+1/2} = \frac{1}{2} \frac{\epsilon_{j+1/2}}{\Delta x} B(-p_{j+1/2}^m) W_2 \frac{\Delta x}{2\epsilon_{j+1/2}} 1^T = W_1(p_{j+1/2}) 1^T, \tag{4.2.90c}
\]

\[
1^T \delta_{j+1/2} = -\frac{1}{2} \frac{\epsilon_{j+1/2}}{\Delta x} B(p_{j+1/2}^c) W_2 \frac{\Delta x}{2\epsilon_{j+1/2}} 1^T = -W_1(p_{j+1/2}) 1^T. \tag{4.2.90d}
\]

Similarly, for charge conservation the result reads

\[
r^T \alpha_{j+1/2} = \frac{p_{j+1/2}^c}{\exp(p_{j+1/2})} \epsilon_{j+1/2} \exp(p_{j+1/2}) r^T = \frac{\epsilon_{j+1/2}}{\Delta x} B(-p_{j+1/2}^c) r^T, \tag{4.2.91a}
\]

\[
r^T \beta_{j+1/2} = \frac{p_{j+1/2}^c}{\exp(p_{j+1/2})} \epsilon_{j+1/2} r^T = \frac{\epsilon_{j+1/2}}{\Delta x} B(p_{j+1/2}^c) r^T, \tag{4.2.91b}
\]

\[
r^T \gamma_{j+1/2} = \frac{1}{2} \frac{\epsilon_{j+1/2}}{\Delta x} B(-p_{j+1/2}^c) W_2 \frac{\Delta x}{2\epsilon_{j+1/2}} r^T = W_1(p_{j+1/2}) r^T, \tag{4.2.91c}
\]

\[
r^T \delta_{j+1/2} = -\frac{1}{2} \frac{\epsilon_{j+1/2}}{\Delta x} B(p_{j+1/2}^c) W_2 \frac{\Delta x}{2\epsilon_{j+1/2}} r^T = -W_1(p_{j+1/2}) r^T. \tag{4.2.91d}
\]

Note, that these eigenvalues describe the discretisation coefficients for a scalar advection-diffusion equation for the species \(\sigma^m\) and \(\sigma^c\). As expected, the discretisation coefficients do not depend on a reaction term, since there is no source term for the species \(\sigma^m\) and \(\sigma^c\).

Next, premultiplying the discretized system with the eigenvectors \(1^T\) and \(r^T\) results in

\[
-\alpha_{j-1/2}\sigma_{j-1}^m + (\alpha_{j+1/2} + \beta_{j-1/2}) \sigma_{j+1/2}^m - \beta_{j+1/2}\sigma_{j+1}^m = 0, \tag{4.2.92a}
\]

\[
-\alpha_{j-1/2}\sigma_{j-1}^c + (\alpha_{j+1/2} + \beta_{j-1/2}) \sigma_{j+1/2}^c - \beta_{j+1/2}\sigma_{j+1}^c = 0, \tag{4.2.92b}
\]

where we have used \(1^T s_j = 0\) and \(r^T s_j = 0\), and defined \(1^T y_j =: \sigma_j^m\) and \(r^T y_j =: \sigma_j^c\) according to \((2.1.10)-(2.2.16)\). From these relations and applying that the diffusive eigenvalues \(\epsilon_{j+1/2}^m\) and \(\epsilon_{j+1/2}^c\) are constant, i.e., \(\epsilon_{j+1/2}^m := \epsilon_m^c\) and \(\epsilon_{j+1/2}^c := \epsilon_c^c\) on each nodal point, it follows that \(\sigma_j^m\) and \(\sigma_j^c\) are weighted averages of its neighbours. Thus, when appropriate boundary conditions are applied such that \(\sigma_j^m = 1\) and \(\sigma_j^c = 0\) hold on the boundary, then the numerical solution obeys discrete mass and charge conservation without discretisation error.

### 4.3 Numerical examples: scalar scheme

In this section the scalar advection-diffusion-reaction schemes are tested. The performance of the scalar ADR-HF and AD-HF schemes, described in section 4.1.4, are compared.

The examples serve to verify the convergence and accuracy of the discretisation for a variety of problems. In general, the accuracy is quantified using the average discretisation error \(e(h) = h ||\varphi - \varphi^*||_1\) with \(\varphi = \varphi(x)\) the numerical solution and \(\varphi^*\) the exact solution restricted to the grid. The first two examples are reproduced from [7] with the author’s permission. Note that in our case the BVP is made dimensionless.
4.3.1 Example 1: boundary layer solution

Consider the following BVP

$$\frac{d}{dx} \left( u \varphi - \varepsilon \frac{d \varphi}{dx} \right) = c \varphi, \quad 0 < \bar{x} < L,$$

$$\varphi(0) = \varphi_L, \quad \varphi(L) = \varphi_R.$$ 

The ODE is made dimensionless by using $\bar{x} = xL$, i.e., we obtain the BVP

$$Pe \frac{d \varphi}{dx} - \frac{d^2 \varphi}{dx^2} = Da \varphi, \quad 0 < x < 1,$$

$$\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R.$$  

For the solution we take boundary conditions $\varphi_L = 0$, $\varphi_R = 2$ and parameters $L = 2$, $u = -1$, $\varepsilon = 10^{-2}$ and $c = 2$. Therefore, the Péclet and diffusive Damköhler numbers are given by $Pe = -2 \cdot 10^2$ and $Da^d = 8 \cdot 10^2$, respectively. The numerical solutions and corresponding discretisation errors are plotted in figure 4.2. For this solution the Péclet and diffusive Damköhler numbers are high and are roughly balanced, i.e., $Da^d = -4$. The ADR-HF scheme is on most grid sizes at least two orders of magnitude more accurate than the AD-HF scheme, while both schemes are second order accurate.

![Figure 4.2: Example 1, boundary layer solution. Numerical and exact solutions with corresponding discretisation errors. Parameter values are: $h^{-1} = 40$, $Pe = -2 \cdot 10^2$, $Da^d = 8 \cdot 10^2$, $\varphi_L = 0$ and $\varphi_R = 2$.](image)

4.3.2 Example 2: oscillatory solution

Consider the same BVP again

$$Pe \frac{d \varphi}{dx} - \frac{d^2 \varphi}{dx^2} = Da \varphi, \quad 0 < x < 1,$$

$$\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R.$$  

For the solution we take boundary conditions $\varphi_L = 0$, $\varphi_R = 2$ and parameters $L = 2$, $u = 1$, $\varepsilon = 0.5$ and $c = 2 \cdot 10^2$. Therefore, the Péclet and Damköhler numbers are given by $Pe = 4$ and $Da^d = 1.6 \cdot 10^3$, respectively. The numerical solutions and corresponding discretisation errors are plotted in figure 4.3. For this solution the Péclet number is moderate and the diffusive Damköhler...
4.3. Numerical examples: scalar scheme

numbers is resulting in a large convective Damköhler number of $\text{Da}^c = 4 \cdot 10^2$. The ADR-HF scheme is on most grid sizes about twice as accurate compared to the AD-HF scheme, while both schemes display second order convergence. Note that the peak at $h^{-1} = 40$ is at a gridspace where the oscillations cannot be represented correctly, where the ADR-HF scheme apparently overshoots more than the AD-HF scheme.

![Graphs](a) numerical and exact solutions (b) discretisation error

Figure 4.3: Example 2, oscillatory solution. Numerical and exact solutions with corresponding discretisation errors. Parameter values are: $h^{-1} = 80$, $\text{Pe} = 4$, $\text{Da}^d = 1.6 \cdot 10^3$, $\varphi_L = 0$ and $\varphi_R = 2$.

4.3.3 Example 3: advection-diffusion limit

Consider the same BVP again

\[
\begin{align*}
\text{Pe} \frac{d\varphi}{dx} - \frac{d^2\varphi}{dx^2} &= \text{Da} \varphi, \\
\varphi(0) &= \varphi_L, \quad \varphi(1) = \varphi_R.
\end{align*}
\]

(4.3.3a) \qquad (4.3.3b)

For the solution we take boundary conditions $\varphi_L = 0$, $\varphi_R = 2$ and parameters $\text{Pe} = 20$ and $\text{Da}^d = 10^{-3}$. The convective Damköhler number for this BVP is $\text{Da}^c = 5 \cdot 10^{-5}$. The numerical solutions and corresponding discretisation errors are plotted in figure 4.4. Since reaction is too low to be important, the solutions are purely an advection-diffusion balance. Therefore, the AD-HF scheme quickly reaches machine-precision, while the ADR-HF scheme only gives a very good approximation to the problem with for the coarse grids an accuracy difference of 5 orders of magnitude compared to the AD-HF scheme.

For this problem $r = \sqrt{1 - 4 \text{Da}^d / \text{Pe}^2} = 0.999995$, therefore, the ADR-HF scheme does not exactly reduce to the AD-HF scheme. The accuracy difference, between ADR-HF and AD-HF, can be remedied by replacing the ADR homogeneous flux with the AD homogeneous flux when $|1 - r| < \zeta$ for a particular choice of $\zeta$, e.g., $\zeta = 10^{-3}$. 

Chapter 4. FVM applied to advection-diffusion-reaction equations

Figure 4.4: Example 3, advection-diffusion limit. Numerical and exact solutions with corresponding discretisation errors. Parameter values are: $h^{-1} = 20$, $Pe = 20$, $Da^d = 10^{-3}$, $\varphi_L = 0$ and $\varphi_R = 2$.

4.4 Numerical examples: system scheme

In this section the system advection-diffusion-reaction schemes are tested. The performance of the system ADR-HF and ADR-CF schemes, described in sections 4.2.1-4.2.2, are compared with the system AD-HF and system AD-CF schemes. The examples serve to verify the convergence and accuracy of the discretisation for a variety of problems.

4.4.1 Example 1: diagonalizable system

In the first example we will consider the following dimensionless BVP

$$\frac{d}{dx} \left( Pe \, \varphi - \frac{d\varphi}{dx} \right) = Da^d \, \varphi, \quad 0 < x < 1,$$

$$\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R,$$

with the Péclet matrix $Pe := E^{-1}UL$ and the diffusive Damkohler matrix $Da^d := E^{-1}CL^2$, where $L$ is some characteristic length scale that normalized the variable $x$. We take the Péclet and diffusive Damkohler matrices such that they commute, i.e.,

$$Pe := V\Lambda V^{-1},$$

$$Da^d := VMV^{-1},$$

where the matrices share the same eigenvectors $V = (v_1, ..., v_m)$, and the matrices $\Lambda = \text{diag}(\lambda_1, ..., \lambda_m)$ and $M = \text{diag}(\mu_1, ..., \mu_m)$ commute. Therefore, the solution of the BVP is given by

$$\varphi(x) = e^{1/2Pe \, x} \sinh \left( \frac{1}{2} Pe \, R \, (1 - x) \right) \left( \sinh \left( \frac{1}{2} Pe \, R \right) \right)^{-1} \varphi_L$$

$$+ e^{-1/2Pe \, (1-x)} \sinh \left( \frac{1}{2} Pe \, Rx \right) \left( \sinh \left( \frac{1}{2} Pe \, R \right) \right)^{-1} \varphi_R,$$

with $R := V \text{diag}(r_1, ..., r_m)V^{-1}$ and $r_i := \sqrt{1 - 4\mu_i/\lambda_i^2}$, cf. (4.1.18).
Coupled reaction and diffusion profiles

First, we consider the example with
\[
V = \begin{pmatrix} 1 & 0 \\ 0.8 & 1 \end{pmatrix}, \quad \Lambda = \text{diag}(10^{-2}, 10^{-2}), \quad M = \text{diag}(-10^2, -10^{-2}),
\]
and boundary conditions
\[
\varphi_L = (0.1, 0.9)^T, \quad \varphi_R = (1, 0)^T.
\]

For \(\varphi_1(x)\) the solution is reaction dominant while for \(\varphi_2(x)\) diffusion is dominant and the second solution is strongly coupled to the first solution. The numerical solutions and discretisation errors are presented in figure 4.5. As expected, the solution for \(\varphi_1(x)\) shows boundary layers near the walls corresponding to a reaction dominant profile. The solution for \(\varphi_2(x)\) is almost a straight line, except near the right wall where a boundary layer is present due to the coupling with \(\varphi_1(x)\). The discretisation errors, computed using \(e_i(h) = ||\varphi_i - \varphi_i^*||_\infty\), show that solutions are already quite accurate for a coarse grid. Both the AD-HF and ADR-HF schemes display second order convergence, with the ADR-HF scheme being slightly more accurate than the AD-HF scheme due to the inclusion of the reaction term in the flux approximation.

**Oscillatory solutions**

Next, we change the parameters such that reactions become more dominant with opposite signs:
\[
V = \begin{pmatrix} 1 & 0.2 \\ 0.01 & 3 \end{pmatrix}, \quad \Lambda = \text{diag}(1, 10^{-2}), \quad M = \text{diag}(-10^2, 10^3),
\]
and boundary conditions
\[
\varphi_L = (0.1, 0.9)^T, \quad \varphi_R = (1, 0)^T.
\]

Both \(\varphi_1(x)\) and \(\varphi_2(x)\) are reaction dominant and due to the positiveness of the reaction coefficient we expect oscillations for \(\varphi_2(x)\) and since the system is coupled, we also expect the oscillations for \(\varphi_1(x)\), see figure 4.6. The amplitude mismatch between the numerical solutions and the exact
solution is for the ADR-HF scheme less than the AD-HF scheme. This better representation for the ADR-HF scheme is confirmed in the discretisation error figure [4.7]. From the discretisation error figure, we notice that the ADR-HF scheme is approximately one order of magnitude more accurate than the AD-HF scheme.

![Graph](image)

(a) $\varphi_1(x)$  

(b) $\varphi_2(x)$

Figure 4.6: Example 1: diagonalizable system. Numerical solutions computed with the ADR-HF and AD-HF schemes and the exact solution for this problem. Parameter values are $h^{-1} = 80$ and other parameters are presented in (4.4.5).

![Graph](image)

Figure 4.7: Example 1: diagonalizable system. Discretisation errors for the ADR-HF and AD-HF schemes. Parameter values are presented in (4.4.5).

### 4.4.2 Example 2: synthesized solution

In this example we consider the dimensionless system BVP with a general source term $s(x)$

\[
\operatorname{Pe} \frac{d\varphi}{dx} - \frac{d^2\varphi}{dx^2} = \text{Da} \ \varphi + s(x), \quad 0 < x < 1, \tag{4.4.6a}
\]

\[
\varphi(0) = \varphi_L, \quad \varphi(1) = \varphi_R. \tag{4.4.6b}
\]
Next we choose a source $s(x)$ such that the exact solution will be
\[
\varphi(x) = \left( e^{-\text{Pe} - I} \right)^{-1} \left( e^{-\text{Pe}(1-x) - I} \right) \varphi_L + \left( \sin \left( \sqrt{\text{Da}^d} \right) \right)^{-1} \sin \left( \sqrt{\text{Da}^d} x \right) \varphi_R. \tag{4.4.7}
\]

For the diffusion, advection and reaction matrices we take
\[
E = \frac{1}{2} \varepsilon \begin{pmatrix} 1 + \alpha & 1 - \alpha \\ 1 - \alpha & 1 + \alpha \end{pmatrix}, \quad U = uI, \quad C = k \text{diag}(1, r), \tag{4.4.8}
\]
respectively. The Péclet and diffusive Damköhler matrices are given by
\[
\text{Pe} = p \begin{pmatrix} 1 + \alpha & -1 + \alpha \\ -1 + \alpha & 1 + \alpha \end{pmatrix}, \quad \text{Da}^d = d \begin{pmatrix} 1 + \alpha & r(-1 + \alpha) \\ -1 + \alpha & r(1 + \alpha) \end{pmatrix}, \tag{4.4.9}
\]
where $p = \frac{1}{2} u a / (\alpha \varepsilon)$ is a Péclet number and $d = \frac{1}{2} k a^2 / (\alpha \varepsilon)$ is a diffusive Damköhler number for a characteristic length scale $a$. We describe the following Dirichlet boundary conditions
\[
\varphi_L = (1, 1)^T, \quad \varphi_R = (0.2, 0.8)^T. \tag{4.4.10}
\]

**Advection and reaction dominant**

First, we take $r = -0.3$. The solutions are advection and reaction dominant with a strong coupling. This is confirmed in the plots of the solutions shown in figure 4.9. There is a slight difference between the numerical solutions and the exact solution, therefore, the plots for the difference between the numerical and exact solution $\Delta \varphi_i(x) = \varphi_i(x) - \varphi^*_i(x)$ is also shown. From the differences we can conclude that for $\varphi_1(x)$ the AD-HF and ADR-CF scheme are roughly equally accurate, while for $\varphi_2(x)$ the ADR-CF scheme is clearly more accurate than the other schemes.

![Figure 4.8: Example 2: synthesized solution with advection and reaction dominant, and strong diffusive coupling. Source terms $s(x)$. Parameter values are $h^{-1} = 20$, $p = 25$, $d = -250$, $\alpha = 0.2$ and $r = -0.3$.](image)
Figure 4.9: Example 2: synthesized solution with advection and reaction dominant, and strong diffusive coupling. Numerical and exact solutions. Parameter values are $h^{-1} = 20$, $p = 25$, $d = -250$, $\alpha = 0.2$ and $r = -0.3$.

These accuracy differences are also confirmed in the discretisation error computed with $e_i(h) = ||\varphi_i - \varphi^*_i||_1$, see figure 4.10. All four schemes display second order convergence, however, the ADR-HF and AD-CF scheme have the lowest accuracy for both $\varphi_1(x)$ and $\varphi_2(x)$. While the AD-HF scheme has roughly the same accuracy as the ADR-CF scheme for $\varphi_1(x)$ and for $\varphi_2(x)$ the ADR-CF scheme is one order of magnitude more accurate than the other schemes. The high accuracy of the AD-HF scheme for $\varphi_1(x)$ can be explained from the profile of the exact solution, since it closely resembles a pure advection-diffusion profile with high Péclet number. For $\varphi_2(x)$ this is not the case, where even a gradient is present in the source terms, see figure 4.8. Although, the reaction terms are somewhat moderate, advection is still important. Therefore, the transport fluxes for the ADR-HF scheme are too much damped by the linear reaction term. This linear reaction term also is the reason why the AD-CF scheme performs worse than the AD-HF scheme. Therefore, the following examples investigates the case were the linear reaction term is not important.
4.4. Numerical examples: system scheme

Figure 4.10: Example 2: synthesized solution with advection and reaction dominant, and strong diffusive coupling. Discretisation errors for the tested schemes. Parameter values are \( h^{-1} = 20 \), \( p = 25 \), \( d = -250 \), \( \alpha = 0.2 \) and \( r = -0.3 \).

Advection-diffusion limit

Next, we set \( d = 0 \), such that \( Da = 0 \). The ODE system reduces to an advection-diffusion system with a general source term that reduces to \( s(x) = Pe \varphi_R \), see figure 4.11. The numerical and exact solutions, and corresponding discretisation errors are shown in figure 4.12. It can be confirmed that flux approximations in the ADR system schemes reduce to the flux approximations for the AD system scheme. The numerical solutions are already obtained at machine precision for coarse grids. Since the source is a constant and is, therefore, integrated exactly with the midpoint rule when deriving the flux balance. The resulting scheme is thus exact up to machine precision.

Figure 4.11: Example 2: synthesized solution in advection-diffusion limit. Source terms \( s(x) \). Parameter values are \( h^{-1} = 20 \), \( p = 25 \), \( d = 0 \) and \( \alpha = 0.2 \).
Figure 4.12: Example 2: synthesized solution in advection-diffusion limit. Numerical and exact solutions, and corresponding discretisation errors for the tested schemes. Parameter values are $h^{-1} = 20$, $p = 25$, $d = 0$ and $\alpha = 0.2$. 

(a) $\varphi_1(x)$ 

(b) $\varphi_2(x)$ 

(c) $\epsilon_1(h)$ 

(d) $\epsilon_2(h)$
Chapter 5

General applications

In this chapter the scalar diffusion-reaction and advection-diffusion-reaction schemes, from chapters 3-4, are applied to general physics problems. For the examples considered here, analytical solutions are available such that the performance of the schemes for physics examples can be verified. The average discretisation error is computed with $e(h) = \| \varphi - \varphi^* \|_\infty$ with $\varphi^*$ the exact solution restricted to the grid.

First an example from quantum mechanics is considered, where we solve a stationary one-dimensional Schrödinger equation with a triangular well potential. Second, a non-linear diffusion-reaction equation is solved that arises in Ginzburg-Landau theory.

5.1 Schrödinger equation with a triangular well

The time-independent Schrödinger equation is given by

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(\bar{x})}{d\bar{x}^2} + V(\bar{x})\Psi(\bar{x}) = E_n \Psi(\bar{x}),$$

where $\hbar = h/(2\pi)$ is the reduced Planck constant, $m$ the electron mass, $\Psi(\bar{x})$ the wavefunction, $V(\bar{x})$ the potential and $E_n$ the electron energy. Consider now a triangular well with constant electric field $E$, such that $V(\bar{x}) = qE\bar{x}$. This type of problem for example occurs in semiconductor devices where the quality of an interface, which matches different alternating grown layers, is studied [25]. Therefore, the problem is formulated as

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(\bar{x})}{d\bar{x}^2} + qE\bar{x}\Psi(\bar{x}) = E_n \Psi(\bar{x}), \quad 0 < \bar{x} < a,$$  

$$\Psi(0) = \Psi_L \quad \Psi(a) = \Psi_R,$$

which can be rewritten to

$$\frac{d^2 \Psi}{dx^2} - \frac{4ma^2}{\hbar^2} E_n \left( \frac{qEa}{E_n} x - \frac{1}{2} \right) \Psi = 0, \quad 0 < x < 1,$$

where $x = \bar{x}/a$ is the dimensionless coordinate. Next, the auxiliary variables $\alpha$ and $\beta$ are defined by

$$\alpha := E_n \left( \frac{4m}{\hbar^2 q^2 E^2} \right)^{1/3}, \quad \beta := \frac{E_n}{qEa}, \quad y := \beta x - \frac{1}{2},$$

such that ODE (5.1.3) can be written as

$$\frac{d^2 \Psi}{dy^2} - \alpha^3 y \Psi = 0.$$
Therefore, the exact solution of (5.1.3) is given by

$$
\Psi(x) = \gamma \text{Ai} \left( \alpha \left( \beta x - \frac{1}{2} \right) \right) + \delta \text{Bi} \left( \alpha \left( \beta x - \frac{1}{2} \right) \right),
$$

(5.1.6)

where Ai(z) and Bi(z) are the Airy functions. The constants \( \gamma \) and \( \delta \) have to be determined from the boundary conditions.

In our example, we neglect the normalization constant of the wavefunction. Furthermore, we set \( \Psi_L = 1 \), due to a certain potential for \( x < 0 \), and \( \Psi_R = 0 \), representing an infinite potential well for \( x > 1 \). Moreover, the parameter \( \alpha^3 \) can be thought of as a diffusive Damköhler number and the parameter \( \beta \) represents the energy of the particle relative to the potential energy from the electric field. We set \( \beta = 1 \) such that there is a turning point at \( x = \frac{1}{2} \).

We consider two cases, \( \alpha^3 = 10^3 \) and \( \alpha^3 = 10^4 \). The obtained numerical solutions and exact solutions are shown in figure 5.1. The CD scheme for \( \alpha^3 = 10^3 \) does not describe the initial behaviour of the solution correctly, as the numerical solution first increases near the left wall while the exact solution should decrease. Furthermore, it overshoots on the minima and maxima of the curves. The DR-HF scheme can more accurately capture the exact solution. For \( \alpha^3 = 10^4 \) the CD and DR-HF scheme both show larger amplitudes compared to the exact solution, while the CD scheme overshoots more than the DR-HF scheme.

The accuracy of the schemes is investigated by computing the discretisation error \( e(h) := ||\phi - \phi^*||_\infty \), where \( \phi^* \) is the exact solution restricted to the grid. The discretisation errors are reported in tables 5.1 for \( \alpha^3 = 10^3 \) and 5.2 for \( \alpha^3 = 10^4 \). As expected, the CD and DR-HF schemes show second order convergence in both cases, while the DR-HF scheme is more accurate. The increased accuracy is computed using \( e_{CD}(h)/e_{DR}(h) \), for which we expect a ratio of 2 for constant coefficients from the theory given in section 3.1. However, we find a slightly higher ratios of 2.04 and 2.15 for \( \alpha^3 = 10^3 \) and \( \alpha^3 = 10^4 \), respectively. This is most likely due to the spatial dependence of the problem.
5.2 Ginzburg-Landau theory for neutral superfluids

In Landau theory of phase transitions a system is described by an order parameter, which is a thermodynamic variable that is zero on one side of a transition and non-zero on the other side. In the case of an electrically neutral superfluid, an order parameter is the macroscopic condensate wave function \( \psi(x) \) which is assumed to be spatially dependent. The Landau functional that includes the simplest term containing gradients and respects the symmetry is given by \[ L[\psi] = \int dx \left[ \alpha \psi^2 + \frac{1}{2} \beta \psi^4 + \gamma \left( \frac{d\psi}{dx} \right)^2 \right], \]

where \( \beta > 0 \) and \( \gamma > 0 \). The Landau functional represents a free energy, therefore a differential equation for \( \psi(x) \) can be derived that minimizes \( L[\psi] \). The differential equation is given by \[ \frac{1}{2} \gamma \psi''(x) + \alpha \psi(x) + \beta \psi^3(x) = 0, \]

where the prime \( ' \) denotes \( \frac{d}{dx} \). By scaling the solution with \( \psi(x) = \sqrt{-\alpha/\beta} \varphi(x) \) and introducing the relevant length scale \( \xi = \sqrt{\gamma/\alpha} \) we find

\[ \frac{1}{2} \xi^2 \varphi''(x) = \varphi^3(x) - \varphi(x), \]

where usually the boundary conditions \( \varphi(0) = 0 \) and \( \varphi'(\infty) = 0 \) are applied. However, we restrict the solution to \( x \in (-a, a) \), therefore we apply the boundary conditions \( \varphi(-a) = \tanh(-a/\xi) \) and
\( \varphi(a) = \tanh(a/\xi) \). The boundary values were found from the exact solution given by \( \varphi(x) = \tanh(x/\xi) \).

The model problem is solved for \( \xi = 0.5 \) and \( \xi = 1 \) using Newton iteration. The obtained numerical solutions and exact solutions are shown in figure 5.2, where the numerical solutions were computed using the CD, DR-HF and DR-CF schemes. The solutions for a very coarse grid are already accurate when computed with the DR-CF schemes.

\[
\begin{align*}
\text{(a) } \xi &= 0.5 \\
\text{(b) } \xi &= 1
\end{align*}
\]

Figure 5.2: The order parameter \( \varphi(x) \) as a function of the coordinate \( x \). Parameter values are: \( h^{-1} = 10 \).

The discretisation error for this problem is shown in figure 5.3. All three schemes show second order convergence in both cases, while the DR-HF scheme is slightly more accurate than the CD scheme and the DR-CF scheme even more accurate. The DR-CF scheme is roughly one order of magnitude more accurate than the CD scheme for \( \xi = 1 \), while for \( \xi = 0.5 \) the increased accuracy is less than one order of magnitude. For these values of \( \xi \) the grid Damköhler number is small enough such that the inhomogeneous flux reduces to \( F_{j+1/2}^j \approx h(s_j - s_{j+1})/8 \). Therefore, the accuracy difference in the DR-CF scheme for the two cases is only due to the smaller gradient in the solution for \( \xi = 1 \) compared to \( \xi = 0.5 \).

\[
\begin{align*}
\text{(a) } \xi &= 0.5 \\
\text{(b) } \xi &= 1
\end{align*}
\]

Figure 5.3: The discretisation error \( e(h) \) for the order parameter \( \varphi(x) \).
Chapter 6

Applications: multicomponent mixtures

In this chapter, the theory of the multicomponent mixtures described in chapter 2 and the numerical schemes obtained in chapters 3-4 are combined to simulate multicomponent mixtures. The mixtures are simulated using only the mass conservation laws for a one-dimensional mixture, which reads

$$\frac{d}{dx} \left( \rho u \nu - \mathcal{E} \frac{dy}{dx} \right) = \text{diag} (m) \omega.$$ 

In this chapter only the homogeneous flux schemes are used, e.g., the DR-HF and ADR-HF schemes, since the reaction rates are at least linear in a species' density. Therefore, the reactions are combined in the linear reaction term \( \text{diag} (m) \omega = Cy \).

In general for these multicomponent mixtures there is no exact solution available, since the diffusion and reaction matrices are non-linear in the species' mass fractions. Therefore, we employ Picard iteration to solve the system. The iteration process is stopped when the change in mass fractions is smaller than some set tolerance, i.e., \( ||y^{k+1} - y^k||_\infty < \text{tol} \) with \( k \) the iteration number. In some examples underrelaxation is employed to restrict the update, given by the symbol urf.

The average discretisation error is computed for a mass fraction \( y_S \) of the \( S \) species with \( e(h) := ||y_S - y^*_S||_\infty \), with \( y^*_S \) a reference solution. If no exact solution is available, this reference solution is obtained by solving the system on a very fine grid.

First, a binary mixture is simulated in order to validate the code. Then, the dissociation of a nitrogen oxide in a nitrogen, oxygen mixture is considered. Finally, the schemes are applied to simulate the influence of aluminium on an argon plasma.

6.1 Test case: binary mixture

In order to validate the written code and the numerical methods we consider a binary mixture of atomic argon and hydrogen, as in [10]. The mixture is confined to a one-dimensional domain with coordinates between \( x_L = 0 \) m and \( x_R = 1 \) m. The considered problem is purely diffusive, i.e. no advection or time dependence. Furthermore, the pressure and temperature are uniform. On the boundaries we describe Dirichlet boundary conditions. The analytical solution to this problem is given by [10, eq. (51)]

$$y_H(x) = (y_{H,L} + \gamma) \left( \frac{y_{H,R} + \gamma}{y_{H,L} + \gamma} \right)^{x/x_R} - \gamma,$$  \hspace{1cm} (6.1.1)

where \( y_{H,L} = 0.99, y_{H,R} = 0.4 \) are the Dirichlet boundary conditions for hydrogen on the left-hand side and right-hand side of the domain, respectively, and \( \gamma = m_H/(m_{Ar} - m_H) \).
Chapter 6. Applications: multicomponent mixtures

The numerical solution is computed using the system variant of the standard central difference (CD) scheme, described in section 3.2.1. The obtained numerical solutions and exact solutions are presented in figure 6.1a. Furthermore, mass conservation is shown in figure 6.1b. As expected there is mass conservation up to machine precision in the system for this diffusive mixture.

The discretisation error \( e(h) \) is computed for the H mass fraction with \( y_H^* \) denoting the analytical solution restricted to the grid. The discretisation error is shown in table 6.1. The discretisation error shows that the solution is accurate up to machine precision for any grid size. This is in contrast with the results shown in [10] where the numerical solution is not accurate up to machine precision for the shown grid spacings. Since the code used by Peerenboom et al. was published, certain differences in implementation can be found. One of the differences is due to the different grid structure, they use a cell centered grid with extra nodal points on the boundaries, while in my code a vertex-centered grid is used. Another difference is due to the interpolation of the diffusion coefficients to the interface, which can be rather important when the diffusion coefficients are not constant over a control volume, as noted in [2], [6] and [27].

![Graph](a) numerical and analytical solutions

![Graph](b) mass conservation

Figure 6.1: Binary mixture consisting of atomic hydrogen and argon. Numerical solution computed on a vertex-centered grid with \( h^{-1} = 20 \). Parameter values are: \( \text{urf} = 1, \text{tol} = 10^{-11} \).

<table>
<thead>
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<th>( N_h )</th>
<th>( e(h) )</th>
</tr>
</thead>
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<tr>
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<td>8.529e-14</td>
</tr>
<tr>
<td>20</td>
<td>1.410e-13</td>
</tr>
<tr>
<td>40</td>
<td>1.995e-13</td>
</tr>
<tr>
<td>80</td>
<td>4.549e-14</td>
</tr>
</tbody>
</table>

### 6.2 The dissociation of NO in a nitrogen-oxygen mixture

Consider a mixture of \( N_2, O_2 \) and NO. The reaction mechanisms in this mixture are usually modelled during combustion, therefore at higher temperatures than room temperature. This causes the nitrogen and oxygen to react to form nitrogen oxide NO, using certain elementary reactions that include the atomic nitrogen N and oxygen O. However, in this example we consider a mixture where already some NO is present at the boundaries of the mixture and the temperature of the mixture
has already dropped to a uniform $T = 300$ K. Since the temperature is already low, we only consider
the following dissociation reaction
\[ 2 \text{NO} \rightarrow \text{N}_2 + \text{O}_2. \] (6.2.1)

The reaction rate for this reaction is found by using detailed balancing and combining elementary
reactions from [28]. The reaction rate is given by the Arrhenius equation (2.3.4) with $A = 1.83 \times 10^{-17}$
$\text{m}^3/\text{s}$, $q = 0.3$, $T_{\text{ref}} = 1$ K and $E_a = 52.5$ kJ/mol. The mixture is confined to a one-dimensional
domain between $x_L = 0$ m and $x_R = 1$ m. The bulk momentum and energy balances of the mixture
are neglected.

6.2.1 No mass flow

First, we consider the mixture at a uniform pressure of $p = 2 \times 10^4$ Pa and without any mass flow,
i.e., $u = 0$ m/s. Therefore, we employ the system diffusion-reaction and system central difference
schemes in order to compute the numerical solution. The Dirichlet boundary conditions for this
mixture are shown in table 6.2.

Table 6.2: The dissociation of NO in a nitrogen-oxygen mixture, without mass flow. The Dirichlet
boundary conditions on the left-hand side $y_{L}$ and right-hand side $y_{R}$ of the domain.

<table>
<thead>
<tr>
<th></th>
<th>$y_{L}$</th>
<th>$y_{R}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>0.4</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>0.4</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>0.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

In figure 6.2 the results are presented. On the left-hand side and right-hand side nitrogenoxide is
present which dissociates quickly, causing the steep gradients in the boundary layers. The mixture
is thus reaction-dominant. In figure 6.2 the mass conservation is plotted and from this figure we can
conclude that there is indeed mass conservation up to machine precision as expected from theory.

(a) mass fractions

(b) mass conservation

Figure 6.2: The dissociation of NO in a nitrogen-oxygen mixture, without mass flow. The solutions
were obtained using the DR-HF scheme on a grid with $N_h = 40$. Parameter values are: $T = 300$ K,
$p = 2 \times 10^4$ Pa, $\text{urf} = 0.7$, $\text{tol} = 10^{-12}$.

In this example we investigate the accuracy of the system DR-HF and CD schemes using the
discretisation error. The discretisation error is found by comparing the numerical solution for $y_{\text{NO}}$
to a numerical solution $y_{\text{NO}}^*$ computed on a fine grid with $N_h = 2560$, that is approximately the
exact solution. The discretisation errors are plotted in figure 6.3a. Both schemes show second order convergence, with the DR-HF scheme being slightly more accurate than the CD scheme. Despite this slightly higher accuracy the DR-HF scheme requires more computation time, see figure 6.3b. This is due to the DR-HF scheme requiring more matrix operations compared to the CD scheme.

Note that for the coarse grid with $N_h = 10$ the DR-HF scheme performs better than the CD scheme, i.e., it is more accurate and requires less computation time. However, the profile of boundary layers cannot be represented correctly since the size of the boundary layer is approximately 0.1 m depending on the species.

![Figure 6.3: The dissociation of NO in a nitrogen-oxygen mixture, without mass flow. The solutions were obtained using the DR-HF and CD scheme. Parameter values are: $T = 300$ K, $p = 2 \cdot 10^4$ K, $urf = 0.7$, $tol = 10^{-12}$.](image)

The discretisation error is also given in table 6.3. The results show the second order convergence for both schemes. The last column indicates the discrisation error relative of the CD scheme to the DR-HF scheme, showing the accuracy increase of the DR-HF scheme. For constant coefficients we expect the ratio to be equal to 2, however since the coefficients are not constant the ratio is approximately 1.3 - 1.4 in the limit $h \to 0$.

<table>
<thead>
<tr>
<th>$N_h$</th>
<th>$e_{DR}(h)$</th>
<th>$e_{DR}(h)/e_{DR}(h/2)$</th>
<th>$e_{CD}(h)$</th>
<th>$e_{CD}(h)/e_{CD}(h/2)$</th>
<th>$e_{CD}(h)/e_{DR}(h)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.305e-02</td>
<td>0.601</td>
<td>4.271e-02</td>
<td>1.110</td>
<td>3.273</td>
</tr>
<tr>
<td>20</td>
<td>2.172e-02</td>
<td>1.440</td>
<td>3.849e-02</td>
<td>1.749</td>
<td>1.772</td>
</tr>
<tr>
<td>40</td>
<td>1.508e-02</td>
<td>2.736</td>
<td>2.200e-02</td>
<td>2.909</td>
<td>1.459</td>
</tr>
<tr>
<td>80</td>
<td>5.511e-03</td>
<td>3.588</td>
<td>7.563e-03</td>
<td>3.649</td>
<td>1.372</td>
</tr>
<tr>
<td>160</td>
<td>1.536e-03</td>
<td>3.920</td>
<td>2.073e-03</td>
<td>3.926</td>
<td>1.349</td>
</tr>
<tr>
<td>320</td>
<td>3.919e-04</td>
<td>4.151</td>
<td>5.279e-04</td>
<td>4.103</td>
<td>1.347</td>
</tr>
<tr>
<td>1280</td>
<td>1.892e-05</td>
<td>2.749e-05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2. The dissociation of NO in a nitrogen-oxygen mixture

6.2.2 Constant mass flow

Next, we consider the same mixture, however, we add a constant mass flow to the system $\rho u = -10^{-3}$ kg/(m$^2$ s) and reduce the pressure of the system to $p = 2 \cdot 10^3$ Pa. The Dirichlet boundary conditions on the left boundary are slightly modified, see table 6.4. We employ the AD-HF and the ADR-HF scheme in order to compute the numerical solution. Due to the imposed mass flow, advection and reaction in the system are balanced, while diffusion is less important.

Table 6.4: The dissociation of NO in a nitrogen-oxygen mixture, with mass flow. The Dirichlet boundary conditions on the left-hand side $y_L$ and right-hand side $y_R$ of the domain.

<table>
<thead>
<tr>
<th></th>
<th>$y_L$</th>
<th>$y_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.4</td>
<td>0.15</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>NO</td>
<td>0.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Due to the mass flow the species are now transported further from the right wall to the left wall before reacting. The obtained numerical solution is shown in figure 6.4a. The results show the formation of a boundary layer at the left wall, due to the dissociation of NO. In figure 6.4b the mass conservation is shown. As expected from theory the discretized system shows mass conservation up to machine precision.

![Image of mass fractions](attachment:image1.png)

![Image of mass conservation](attachment:image2.png)

(a) mass fractions  
(b) mass conservation

Figure 6.4: The dissociation of NO in a nitrogen-oxygen mixture, with mass flow. The solutions were obtained using the ADR-HF scheme on a grid with $N_h = 40$. Parameter values are: $\rho u = -10^{-3}$ kg/(m$^2$ s), $T = 300$ K, $p = 2 \cdot 10^3$ Pa, $urf = 1$, $tol = 10^{-12}$.

Next, we investigate the accuracy of the system ADR-HF and AD-HF schemes by, again, employing the same strategy for determining the discretisation error. The discretisation errors are plotted in figure 6.5a. Both schemes show second order convergence, with the ADR-HF scheme being at last one order of magnitude more accurate than the AD-HF scheme. Since the ADR-HF scheme requires more computations, due to computing the flux from a double-sized matrix instead of direct diagonalization of the Péclet matrix in the case of the AD-HF scheme. Therefore, the computation time is shown as a function of the discretisation error in figure 6.5b. The ADR-HF scheme apparently requires 4 times fewer grid points to achieve the same order of accuracy in less time, compared to the AD-HF scheme, for this example.

Note that the underrelaxation factor for this problem has been set to $urf = 1$, instead of the $urf = 0.7$ for the case where no mass flow is present. This is due to the high enough advective
transport of the NO species such that it cannot react quickly enough in order to let its mass fraction get close to 0.

![Graph](image)

(a) discretisation errors

Figure 6.5: The dissociation of NO in a nitrogen-oxygen mixture, with mass flow. The solutions were obtained using the ADR-HF scheme. Parameter values are: \( \rho u = -10^{-3} \text{ kg/(m}^2\text{s)} \), \( T = 300 \text{ K} \), \( p = 2 \cdot 10^3 \text{ Pa} \), \( \text{urf} = 1 \), \( \text{tol} = 10^{-12} \).

6.3 Ambipolar Ar-Al plasma

In this example we will investigate the effects of aluminium on an argon plasma [29]. Typically this occurs when the argon plasma sputters an aluminium surface, however, in our example we consider the aluminium vapor to be present on the right boundary. Then, the effect of this aluminium vapor on the argon plasma is investigated in steady-state when a gas flow is present and without a gas flow.

The mixture consists of 6 species [29]:

- argon atoms in the ground state Ar;
- excited argon atoms \( \text{Ar}^* \);
- ionized argon atoms \( \text{Ar}^+ \);
- aluminium atoms in the ground state \( \text{Al} \);
- ionized aluminium atoms \( \text{Al}^+ \);
- electrons \( \text{e}^- \).

The plasma is considered quasi-neutral, i.e., \( n_{\text{e}^-} = n_{\text{Ar}^+} + n_{\text{Al}^+} \). The diffusion of the charged species is changed due to ambipolar diffusion. The diffusion coefficients of positive ions are increased, while the diffusion coefficient of electrons is decreased. Furthermore, the reactions that can occur are shown in the table 6.5. Note that the direct ionization rate for Al is much higher, than the direct ionization rate for Ar. This is because the ionization energy for Al is much lower compared to Ar, i.e., 5.99 eV and 15.76 eV respectively.
6.3. Ambipolar Ar-Al plasma

Table 6.5: Ambipolar Ar-Al plasma. The reaction set of the model. The electron temperature \( \hat{T}_e \) is in electronvolt and the rate coefficients are in \( m^3(N_r-1)/s \) with \( N_r \) the number of reactants in the reaction. Source for the reactions rates [30]. The rates for Ar and Al recombination are found from detailed balancing.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar ionization: ( \text{Ar} + e^- \rightarrow \text{Ar}^+ + 2e^- )</td>
<td>( 2.3 \cdot 10^{-14} \hat{T}_e^{0.68} \exp \left(-15.76/\hat{T}_e\right) )</td>
</tr>
<tr>
<td>Ar recombination: ( \text{Ar}^+ + 2e^- \rightarrow \text{Ar} + e^- )</td>
<td>( 8.75 \cdot 10^{-39} \hat{T}_e^{-4.5} )</td>
</tr>
<tr>
<td>Ar excitation: ( \text{Ar} + e^- \rightarrow \text{Ar}^* + e^- )</td>
<td>( 5.0 \cdot 10^{-15} \hat{T}_e^{0.74} \exp \left(-11.56/\hat{T}_e\right) )</td>
</tr>
<tr>
<td>Ar excited ionization: ( \text{Ar}^* + e^- \rightarrow \text{Ar}^+ + 2e^- )</td>
<td>( 6.8 \cdot 10^{-15} \hat{T}_e^{0.67} \exp \left(-4.20/\hat{T}_e\right) )</td>
</tr>
<tr>
<td>Ar de-excitation: ( \text{Ar}^* + e^- \rightarrow \text{Ar} + e^- )</td>
<td>( 4.3 \cdot 10^{-16} \hat{T}_e^{0.74} )</td>
</tr>
<tr>
<td>Ar radiative decay: ( \text{Ar}^* \rightarrow \text{Ar} + h\nu )</td>
<td>( 3.15 \cdot 10^8 )</td>
</tr>
<tr>
<td>Al ionization: ( \text{Al} + e^- \rightarrow \text{Al}^+ + 2e^- )</td>
<td>( 1.23 \cdot 10^{-13} \exp \left(-7.23/\hat{T}_e\right) )</td>
</tr>
<tr>
<td>Al recombination: ( \text{Al}^+ + 2e^- \rightarrow \text{Al} + e^- )</td>
<td>( 1.22 \cdot 10^{-40} \hat{T}_e^{-1.5} )</td>
</tr>
<tr>
<td>Al Penning ionization: ( \text{Ar}^* + \text{Al} \rightarrow \text{Al}^+ + \text{Ar} + e^- )</td>
<td>( 5.9 \cdot 10^{-16} )</td>
</tr>
<tr>
<td>Ar-Al charge exchange: ( \text{Ar}^+ + \text{Al} \rightarrow \text{Al}^+ + \text{Ar} )</td>
<td>( 1.0 \cdot 10^{-15} )</td>
</tr>
</tbody>
</table>

The ambipolar plasma is confined to a one-dimensional domain between \( x_L = 0 \) mm and \( x_R = 0.2 \) mm. The ambipolar plasma mainly consists of argon and its excited species. In addition, at the right-hand side wall a large quantity of aluminium vapor is present, resulting in a constant aluminium mass fraction at the wall. The Dirichlet boundary conditions for this problem are listed in table 6.6. Furthermore, the temperature \( T = T_e = T_h = 8000 \) K and pressure \( p = 10^3 \) Pa are uniform. Consistent with the formulation of the Stefan-Maxwell equations in section 2.4, the heavy particle temperature \( T_h \) was chosen equal to electron temperature \( T_e \) which is quite unrealistic for the considered plasma. Additionally, the bulk momentum and energy balances of the species in the plasma are also neglected. Despite these unrealistic conditions, the applicability and performance of the schemes can still be tested.

Table 6.6: Ambipolar Ar-Al plasma. The Dirichlet boundary conditions on the left-hand side \( y_L \) and right-hand side \( y_R \) of the domain.

<table>
<thead>
<tr>
<th>( y_i )</th>
<th>( y_{i,L} )</th>
<th>( y_{i,R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.99 - 2 \cdot 10^{-5} - 10^{-9}</td>
<td>0.899 - 10^{-9} - 10^{-5}</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>Ar²⁺</td>
<td>10⁻⁵</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>Al</td>
<td>10⁻⁵</td>
<td>0.1</td>
</tr>
<tr>
<td>Al⁺</td>
<td>10⁻⁹</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

6.3.1 No mass flow

First, we consider the ambipolar plasma without any mass flow, i.e., \( u = 0 \) m/s. Therefore, we employ the system DR-HF and CD schemes in order to compute the numerical solution. The
obtained numerical solutions are shown in figure 6.6. The solutions show a somewhat balance between diffusion and reaction, as is evident from the profiles for Ar$^+$ and Al$^+$. The profiles show “boundary layers” that extend almost up to the center of the domain. Furthermore, the ionization fraction is relatively high.

Moreover, the numerical solution, see figure 6.6d, shows that there is mass conservation and charge conservation up to machine precision as expected.

Figure 6.6: Ambipolar Ar-Al plasma, without mass flow. The solutions were obtained using the DR-HF scheme on a grid with $N_h = 40$. Parameter values are: $T = 8000$ K, $p = 10^3$ Pa, urf = 1, tol = $10^{-9}$.

Again, we investigate the accuracy of the system DR-HF and CD schemes using the discretisation error, by comparing the numerical solution to a numerical solution computed on a very fine grid. The discretisation errors are plotted in figure 6.7a calculated for both the Ar$^*$ and Ar$^+$ species. For Ar$^+$ both methods are equally accurate since the Ar$^+$ does not have a steep gradient due to reactions like Ar$^*$ has, therefore the DR-HF scheme is slightly more accurate for representing the Ar$^*$ species. The solutions show, again, that the DR-HF scheme is computationally more expensive than the CD scheme.
6.3. Ambipolar Ar-Al plasma

Figure 6.7: Ambipolar Ar-Al plasma, without mass flow. The solutions were obtained using the DR-HF and CD scheme. Parameter values are: \( T = 8000 \) K, \( p = 10^3 \) Pa, \( \text{urf} = 1 \), \( \text{tol} = 10^{-9} \).

6.3.2 Mass flow - advection and reaction balanced

Next, we consider the same ambipolar plasma, however, we add a constant mass flow to the system \( \rho u = 10 \) kg/(m\(^2\) s). Therefore, we employ the system ADR-HF and AD-HF schemes in order to compute the numerical solution. The obtained numerical solutions are shown in figure 6.8. By adding the constant mass flow, the species are now transported to the right wall. Therefore, there is fewer ion production as is evident from the ionization fraction and the profiles of \( \text{Ar}^+ \) and \( \text{Al}^+ \). This results in the plasma on the left-hand side of the domain being only slightly disturbed by the aluminium vapor.
Figure 6.8: Ambipolar Ar-Al plasma, with mass flow - advection and reaction balanced. The solutions were obtained using the ADR-HF scheme on a grid with $N_h = 40$. Parameter values are: $ho u = 10$ kg/(m$^2$ s), $T = 8000$ K, $p = 10^3$ Pa, $urf = 1$, $tol = 10^{-9}$.

The discretisation errors for the system ADR-HF and AD-HF schemes is shown in figure 6.9a. Both schemes show second order convergence, while the ADR-HF scheme is one order of magnitude more accurate than the AD-HF scheme. The ADR-HF scheme requires fewer gridpoints to achieve the same order of accuracy compared to the AD-HF scheme, see figure 6.9b.
6.3.3 Mass flow - advection dominated

Next, we increase the mass flow of the system to $\rho u = 10^2$ kg/(m$^2$ s) and change the boundary conditions at the right wall, such that more Al is present. The new Dirichlet boundary conditions can be found in table 6.7. Again, we employ the system ADR-HF and AD-HF schemes in order to compute the numerical solution.

Table 6.7: Ambipolar Ar-Al plasma, advection dominated flow. The Dirichlet boundary conditions on the left-hand side $y_{L}$ and right-hand side $y_{R}$ of the domain.

<table>
<thead>
<tr>
<th></th>
<th>$y_{L}$</th>
<th>$y_{R}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ar}$</td>
<td>$0.99 - 2 \cdot 10^{-9} - 10^{-9}$</td>
<td>$0.799 - 10^{-5} - 10^{-5}$</td>
</tr>
<tr>
<td>$\text{Ar}^+$</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>$\text{Ar}^{2+}$</td>
<td>$10^{-5}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>$\text{Al}$</td>
<td>$10^{-5}$</td>
<td>0.2</td>
</tr>
<tr>
<td>$\text{Al}^{3+}$</td>
<td>$10^{-9}$</td>
<td>$10^{-6}$</td>
</tr>
</tbody>
</table>

By changing the boundary conditions at the right wall and increasing the mass flow, the system is less reactive compared to the previous example. Therefore, a smaller boundary layer near the right wall is present and there is much less ionization. Thus, the plasma is even less disturbed by the aluminium vapor, see figure 6.10.
Figure 6.10: Ambipolar Ar-Al plasma, with mass flow - advection and reaction balanced. The solutions were obtained using the ADR-HF scheme on a grid with $N_h = 40$. Parameter values are: $\rho u = 10^2$ kg/(m$^2$ s), $T = 8000$ K, $p = 10^3$ Pa, $\text{urf} = 1$, $\text{tol} = 10^{-9}$.

The discretisation error and computation times of the ADR-HF and AD-HF schemes are shown in figures 6.11a - 6.11b. Since reaction is not dominant, the ADR-HF scheme reduces to the AD-HF scheme, although at a higher computational cost.
Figure 6.11: Ambipolar Ar-Al plasma, with mass flow - advection and reaction balanced. The solutions were obtained using the ADR-HF and AD-HF scheme. Parameter values are: \( \rho u = 10^2 \) \( \text{kg}/(\text{m}^2 \text{s}) \), \( T = 8000 \) K, \( p = 10^3 \) Pa, urf = 1, tol = \( 10^{-9} \).
Chapter 7

Conclusions

The aim of this work is to investigate the inclusion of a linear reaction term in the discretisation of conservation laws, either scalar or in system form. Therefore, complete flux schemes have been derived for diffusion-reaction type conservation laws and for advection-diffusion-reaction type conservation laws. The inclusion of the linear reaction term leads to modified transport fluxes if the linear reaction term becomes dominant with respect to the transport terms, i.e., for high Damköhler numbers. Furthermore, the schemes are shown to reduce to their respective schemes in the limits where advection or reaction are absent.

The scalar and system diffusion-reaction homogeneous flux schemes were shown to display second order convergence, uniform in all Damköhler numbers. Moreover, the scalar homogeneous flux scheme for constant coefficients was shown to be twice as accurate compared to the standard central difference scheme. The inclusion of the inhomogeneous flux in the scalar scheme was shown to improve the accuracy of the scheme, in case a source term is present, although in a rare case the standard central difference scheme outperforms both the scalar homogeneous and complete flux schemes. The system DR-HF scheme was also applied to simulate reacting multicomponent mixtures, including an ambipolar Ar-Al plasma. Consequently, we conclude that the numerical solutions computed with the system DR-HF scheme are physically correct. Analytically and numerically, it was proven that the scheme exhibits mass and charge conservation without discretisation error. Moreover, the scheme displays a higher accuracy compared to the system variant of the CD scheme for the same number of gridpoints, although, a higher computation time is required in order to achieve the same accuracy.

The scalar and system advection-diffusion-reaction homogeneous flux schemes were shown to display second order convergence for various Péclet and Damköhler numbers. The scalar ADR-HF scheme was shown to have increased accuracy over the AD-HF scheme, for several cases. The accuracy increase can be several orders of magnitude depending on the Péclet and Damköhler number. The opposite is also true in rare cases where the accuracy decreases for advection dominated problems with a low Damköhler number, although this can be remedied by replacing the ADR flux with the AD flux in the appropriate limit. Both the system ADR-HF and ADR-CF scheme exhibit second order convergence, furthermore, the ADR-CF scheme has higher accuracy than the AD-HF, AD-CF and ADR-HF schemes. The system ADR-HF scheme was also applied to simulate reacting multicomponent mixtures. We conclude that the numerical solutions computed with the system ADR-HF scheme are physically correct and, moreover, it was proven that the scheme exhibits mass and charge conservation without discretisation error. The ADR-HF scheme displays a higher accuracy compared to the AD-HF scheme, when reactions are important, and reduces to the AD-HF scheme, when reactions are negligible. The ADR-HF scheme also requires fewer gridpoints compared to the AD-HF scheme in order to achieve the same accuracy, additionally with a lower computation time.

To conclude, the inclusion of the linear reaction term in the discretisation leads to improved accuracy in case the linear reaction term is important. Although, for diffusion-reaction systems this
can come at the expense of extra computation time, while for advection-diffusion-reaction systems this leads to increased performance, both in memory usage and computation time.
Chapter 8

Future research

In section 3.2 the DR-CF scheme for systems was derived, however, the scheme’s performance was not tested nor was the scheme applied in any case. Similarly, the scalar ADR-CF scheme from section 4.1 was not applied. The multicomponent mixtures were assumed stationary, although, they can be time-dependent. Therefore, the schemes should be extended to include the time derivative. An example of such an extension can be found in [1]. The advection-diffusion transient complete flux (AD-TCF) presented in the paper uses the matrix coefficients for the inhomogeneous flux in order to find a better approximation for the time derivative, since the time derivative is included in the source term. The resulting time derivative has a three-point coupling in one dimension. In the simulation of the multicomponent mixtures the reactions lead to a linear reaction term and no general source term. The inhomogeneous flux was, therefore, not used in the simulations. However, the matrix coefficients for the inhomogeneous flux can still be used to include the transient behaviour of the solution. Moreover, the schemes should be extended to include higher spatial dimensions. In order to provide more insights in the schemes, stability and convergence for the scalar DR-CF and ADR-CF schemes should be proven.

The linear reaction term and the general source term can, for example in multicomponent mixtures, be freely chosen. In our case all the reactions were included in the linear reaction term. However, all the reactions or some of them can be moved to the general source term, such that the inhomogeneous flux can be included. This freedom in choosing the source term was not explored in this thesis.

The flux approximation for the system ADR schemes is quite unusual, since we cannot separate the Pécelt matrix and Damköhler matrix parts in the derivation. Therefore, the physical significance of the expression is unclear. Moreover, we assumed the submatrix $E_{12}(\Delta x)$ to be regular but did not prove this is the case in general. Investigating whether this is true can lead to better insights in the flux approximation and perhaps a better expression for the flux approximation. The terms in the flux approximation are not numerically feasible to compute when the matrix $A\Delta x$ has an eigenvalue $\lambda_m > 709$, since then the value of $\exp(\lambda_m)$ is too large for the double-precision float on a regular computer.

Finally, the simulated multicomponent mixtures did not include the energy balance, nor, the bulk momentum balance. The conditions for the considered plasma were also quite unrealistic, although providing insights into the performance of the numerical schemes. Simulating these mixtures under more realistic conditions and including the energy and bulk momentum balances may lead to physical insights of the considered multicomponent mixtures.
Appendix A

Scheme overview

The finite volume method can be applied to the different types of conservation laws, either scalar or in system form. Here, an overview of the resulting discretized scheme with flux balances and flux approximations are given. First, in the scalar case the following auxiliary variables are defined

\[ P = \frac{u}{\varepsilon} \Delta x, \quad (A.0.1) \]
\[ D = \frac{|c|}{\varepsilon} (\Delta x)^2, \quad (A.0.2) \]
\[ r = \sqrt{1 - 4 \frac{D}{P^2}}. \quad (A.0.3) \]

Here, \( P \) and \( D \) are the Péclet and Damköhler grid numbers, and the variable \( r \) might become imaginary in case \( \frac{D}{P^2} > \frac{1}{4} \). Furthermore,

\[ \nu = \begin{cases} 
1 & \text{if } c < 0, \\
i & \text{if } c > 0. 
\end{cases} \quad (A.0.4) \]

Also, the following auxiliary functions are needed

\[ B(z) = \frac{z}{e^z - 1}, \quad (A.0.5) \]
\[ W(z) = \frac{e^z - z - 1}{z (e^z - 1)}, \quad (A.0.6) \]
\[ \sinhc(z) = \frac{\sinh(z)}{z}, \quad (A.0.7) \]
\[ \tanhc(z) = \frac{\tanh(z)}{z}, \quad (A.0.8) \]
\[ C(P; r) = e^{P(1-2r)/4} \left( \cosh \left( \frac{1}{4} Pr \right) + \frac{1}{4} P \sinhc \left( \frac{1}{4} Pr \right) \right), \quad (A.0.9) \]
\[ I(P; r) = \frac{4}{P^2 r (r^2 - 1)} \left[ e^{-P/4} \left( \sinh \left( \frac{1}{4} Pr \right) + r \cosh \left( \frac{1}{4} Pr \right) \right) - r \right]. \quad (A.0.10) \]

Furthermore, the subscript \( u,j+1/2 \) denotes the upwind value for a variable for some advection velocity \( u \), i.e.,

\[ \varphi_{u,j+1/2} = \begin{cases} 
\varphi_j & \text{if } u \geq 0, \\
\varphi_{j+1} & \text{if } u < 0. 
\end{cases} \quad (A.0.11) \]

The flux balances for the different types of conservation laws can be summarized as

\[ F_{j+1/2} - F_{j-1/2} = \Delta x (c_j \varphi_j + s_j), \quad (A.0.12) \]
if a linear reaction term is present, or

\[ F_{j+1/2} - F_{j-1/2} = \Delta x s_j, \]  

(A.0.13)

if the linear reaction term can be neglected. The scheme overview for scalar equations, where we have assumed that the coefficients are constant, is given in table A.1.

For the system of conservation laws, the following auxiliary variables are introduced

\[ P = \mathcal{E}^{-1}U \Delta x, \]  

(A.0.14)

\[ D = \mathcal{E}^{-1}C (\Delta x)^2, \]  

(A.0.15)

\[ \hat{P} = \mathcal{E} P \mathcal{E}^{-1}, \]  

(A.0.16)

\[ \hat{D}^2 = -D, \]  

(A.0.17)

where \( P \) and \( D \) are the Péclet matrix and Damköhler matrix. The matrices \( \hat{P} \) and \( \hat{D} \) are auxiliary matrices related to the Péclet and Damköhler matrices. In the derivation of the numerical fluxes the Péclet and Damköhler matrices are assumed to have a complete set of eigenvectors. For any matrix \( A \in \mathbb{R}^{m \times m} \) with a complete set of eigenvectors, the spectral decomposition is given by

\[ A = V \Lambda V^{-1}, \quad \Lambda := \text{diag} (\lambda_1, \lambda_2, ..., \lambda_m), \quad V := (v_1 \, v_2 \, ... \, v_m), \]  

(A.0.18)

then any matrix function \( g(A) \) can be computed with

\[ g(A) = V g(\Lambda) V^{-1}, \]  

(A.0.19a)

\[ g(\Lambda) = \text{diag} (g(\lambda_1), g(\lambda_2), ..., g(\lambda_m)). \]  

(A.0.19b)

Using this spectral decomposition the subscript \( u,j+1/2 \) for a vector is modified. Since the advection velocities are intertwined, the expressions become more complex. For the advection-diffusion scheme \( s_{u,j+1/2} \) is given by

\[ s_{u,j+1/2} = \frac{1}{2} (I + \sigma) s_j + \frac{1}{2} (I - \sigma) s_{j+1}, \quad \sigma = \text{sgn} (\hat{P}). \]  

(A.0.20)

For the advection scheme the upwind values are given by

\[ (U \varphi)_{u,j+1/2} = \frac{1}{2} (I + \sigma) s_j + \frac{1}{2} (I - \sigma) s_{j+1}, \]  

(A.0.21a)

\[ s_{u,j+1} = \frac{1}{2} (I + \sigma) s_j + \frac{1}{2} (I - \sigma) s_{j+1}, \]  

(A.0.21b)

with \( \sigma \) given by

\[ \sigma = \text{sgn} (U). \]  

(A.0.21c)

The flux balances for the different types of conservation laws can be summarized as

\[ F_{j+1/2} - F_{j-1/2} = \Delta x (C_j \varphi_j + s_j), \]  

(A.0.22)

if a linear reaction term is present, or

\[ F_{j+1/2} - F_{j-1/2} = \Delta x s_j, \]  

(A.0.23)

if the linear reaction term can be neglected. The scheme overview for the system of equations, where we have assumed that the coefficients matrices are constant, is given in table A.2.
Table A.1: Scheme overview - scalar equations with constant coefficients.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Flux approximations</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{d}{dx}(u \varphi - \varepsilon \frac{d \varphi}{dx}) = c \varphi + s$</td>
<td>$F^h_{j+1/2} = \frac{\varepsilon}{\Delta x} \left( C(P; r) B(-Pr) \varphi_j - C(-P; r) B(Pr) \varphi_{j+1} \right)$</td>
<td>[7] and sec. 4.1</td>
</tr>
<tr>
<td></td>
<td>$F^i_{j+1/2} = \Delta x \left( C(P; r) B(-Pr) I(P; r) s_j - C(-P; r) B(Pr) I(-P; r) s_{j+1} \right)$</td>
<td></td>
</tr>
<tr>
<td>$\frac{d}{dx}(u \varphi - \varepsilon \frac{d \varphi}{dx}) = s$</td>
<td>$F^h_{j+1/2} = \frac{\varepsilon}{\Delta x} \left( B(-P) \varphi_j - B(P) \varphi_{j+1} \right)$</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>$F^i_{j+1/2} = \Delta x \left( \frac{1}{2} - W(P) \right) s_{n,j+1/2}$</td>
<td></td>
</tr>
<tr>
<td>$-\frac{d}{dx}(\varepsilon \frac{d \varphi}{dx}) = c \varphi + s$</td>
<td>$F^h_{j+1/2} = -\frac{\varepsilon}{\Delta x} \frac{\varphi_{j+1} - \varphi_j}{\sinh \left( \frac{1}{2} \nu \sqrt{D} \right)}$</td>
<td>sec. 3.1</td>
</tr>
<tr>
<td></td>
<td>$F^i_{j+1/2} = \Delta x \left( \frac{s_j - s_{j+1}}{8} \right) \tanh \left( \frac{1}{4} \nu \sqrt{D} \right)$</td>
<td></td>
</tr>
<tr>
<td>$\frac{d}{dx}(u \varphi) = c \varphi + s$</td>
<td>$F^h_{j+1/2} = -\frac{\varepsilon}{\Delta x} (\varphi_{j+1} - \varphi_j)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F^i_{j+1/2} = \Delta x \left( \frac{s_j - s_{j+1}}{8} \right)$</td>
<td></td>
</tr>
<tr>
<td>$-\frac{d}{dx}(\varepsilon \frac{d \varphi}{dx}) = s$</td>
<td>$F^h_{j+1/2} = (u \varphi)_{n,j+1/2}$</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>$F^i_{j+1/2} = \Delta x \left( \frac{1}{2} s_{n,j+1/2} \right)$</td>
<td></td>
</tr>
</tbody>
</table>
Table A.2: Scheme overview - system of equations with constant matrix coefficients.

<table>
<thead>
<tr>
<th>Source</th>
<th>Flux approximations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sec. 3.2</td>
<td>$s = \left( \frac{\frac{\partial p}{\partial p} \cdot \frac{\partial p}{\partial s}}{\frac{\partial p}{\partial p} \cdot \frac{\partial p}{\partial s}} \right)$ $\frac{\partial p}{\partial s}$</td>
</tr>
<tr>
<td>Sec. 4.2</td>
<td>$s = \left( \frac{\frac{\partial p}{\partial p} \cdot \frac{\partial p}{\partial s}}{\frac{\partial p}{\partial p} \cdot \frac{\partial p}{\partial s}} \right)$ $\frac{\partial p}{\partial s}$</td>
</tr>
</tbody>
</table>

System of equations:

\[
d_{1}^{+} \sum_{1}^{+} x \nabla \phi = \frac{1}{1} \left( U \phi - E d \phi \right) = \frac{1}{1} \left( U \phi - E d \phi \right)
\]

\[
s = (\phi \Omega) \frac{xp}{p}
\]
Appendix B

Additional information

B.1 Block matrix properties

B.1.1 Block matrix inversion

The block matrix inversion is given by

\[
\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} A^{-1} + A^{-1}B(D - CA^{-1}B)^{-1}CA^{-1} & -A^{-1}B(D - CA^{-1}B)^{-1} \\ -(D - CA^{-1}B)^{-1}CA^{-1} & (D - CA^{-1}B)^{-1} \end{pmatrix}, \quad (B.1.1)
\]

\[
\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & - (A - BD^{-1}C)^{-1}BD^{-1} \\ -D^{-1}C(A - BD^{-1}C)^{-1} & D^{-1} + D^{-1}C(A - BD^{-1}C)^{-1}BD^{-1} \end{pmatrix}. \quad (B.1.2)
\]

For the second identity we require \( D \) and \( A - BD^{-1}C \) to be regular. If in addition the matrices \( A, B, C \) are also regular, then the block matrix inversion can be rewritten to

\[
\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & - (A - BD^{-1}C)^{-1}BD^{-1} \\ (B - AC^{-1}D)^{-1} & (D - CA^{-1}B)^{-1} \end{pmatrix}. \quad (B.1.3)
\]

B.1.2 Properties of matrix \( A \)

The block matrix \( A \) as in section 4.2 is given by

\[
A = \begin{pmatrix} \mathcal{E}^{-1}U & -\mathcal{E}^{-1} \\ C & 0 \end{pmatrix}. \quad (B.1.4)
\]

The rank of the block matrix \( A \) can be found from the identity [31] eq. (1.3) \[32] eq. (8.11)]

\[
\text{rank} \begin{pmatrix} A & B \\ C & 0 \end{pmatrix} = \text{rank}(B) + \text{rank}(C) + \text{rank}(\mathcal{E} B \mathcal{F} C), \quad (B.1.5)
\]

with

\[
E_A = I - AA^+, \quad F_A = I - A^+A,
\]

where \( A^+ \) is the Moore-Penrose inverse of the matrix \( A \). If a matrix \( A \) is invertible then \( A^+ = A^{-1} \). Furthermore the following identities hold for \( \mathcal{E} \in \mathbb{R}^{m \times m} \)

\[
\text{rank}(\mathcal{E}^{-1}) = \text{rank}(\mathcal{E}) = m, \quad E_{-\mathcal{E}^{-1}} = I - \mathcal{E}^{-1} = 0.
\]
From the above relations the rank of the block matrix $A$ is thus given by

$$\text{rank}(A) = \text{rank}(E^{-1}) + \text{rank}(C) + \text{rank}(E^{-1}UC)$$

$$= m + \text{rank}(C) + \text{rank}(0),$$

(B.1.6)

Note that $\phi \in \mathbb{R}^m$, $v \in \mathbb{R}^{2m}$ and therefore the matrix $A \in \mathbb{R}^{2m \times 2m}$ has $2m$ eigenvalues and eigenvectors. The matrix $A$ is given by

$$A = \begin{pmatrix} E^{-1}U & -E^{-1} \\ C & 0 \end{pmatrix}.$$  

(B.1.7)

The general formula for the determinant of a block matrix, where the matrix $D$ can be inverted, with equal sizes can be found using

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = |D| |A - BD^{-1}C|.$$  

(B.1.8)

The eigenvalues of the matrix $A$ can thus be found using

$$|A - \lambda I_{2m \times 2m}| = |\lambda I_{m \times m}| \left| (E^{-1}U - \lambda I_{m \times m}) + E^{-1}(-\lambda I_{m \times m})^{-1}C \right|$$

$$= |\lambda^2 I_{m \times m} - \lambda E^{-1}U + E^{-1}C| = 0.$$  

(B.1.9)

This problem is the so-called quadratic eigenvalue problem (QEP). For more details on this problem see [23] or [24].
Appendix C

System
advection-diffusion-reaction scheme
- alternative derivation

In this appendix an alternative derivation of the numerical flux for a coupled advection-diffusion-reaction system is presented. The derivation uses a different assumption then the derivation presented in section 4.2.

We consider the following system boundary value problem

\[
\frac{d}{dx} \left( U\varphi - \mathcal{E} \frac{d\varphi}{dx} \right) = C\varphi + s(\varphi), \quad x_j < x < x_{j+1},
\]

\[\varphi(x_j) = \varphi_j, \quad \varphi(x_{j+1}) = \varphi_{j+1},\]

where \( U \) is the advection matrix, \( \mathcal{E} \) the positive definite diffusion matrix and \( C\varphi + s(\varphi) \) represents the complete source, with \( C\varphi \) the linear part of the source. We assume that the matrices \( U, \mathcal{E} \) and \( C \) are constant. The system consists of \( m \) coupled ODE equations, i.e. \( \varphi \in \mathbb{R}^m, \mathcal{E} \in \mathbb{R}^{m \times m} \) etc. We define the flux as

\[ f = U\varphi - \mathcal{E} \frac{d\varphi}{dx}, \]

such that \( \frac{df}{dx} = C\varphi + s(\varphi) \). Next we introduce the vectors \( q = (\varphi, f)^T \in \mathbb{R}^{2m} \) and \( b = (0, s(\varphi))^T \in \mathbb{R}^{2m} \) such that

\[ q' = Aq + b, \quad A = \begin{pmatrix} \mathcal{E}^{-1}U & -\mathcal{E}^{-1}C \\ \Phi_1 & F_1 \end{pmatrix}, \]

with boundary conditions

\[ B_Lq(x_j) + B_Rq(x_{j+1}) = \begin{pmatrix} \varphi_j \\ \varphi_{j+1} \end{pmatrix} =: r, \]

\[ B_L = \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix}, \quad B_R = \begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix}. \]

In the above definitions of the matrices \( B_L, B_R \) the matrices are partitioned into 4 equal-sized submatrices of size \( m \times m \). The fundamental matrix \( Q \) can then be introduced such that

\[ Q' = AQ, \quad Q = \begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}. \]

Therefore the boundary conditions for \( Q \) are given by \( B_LQ(x_j) + B_RQ(x_{j+1}) = I \). In the above relation \( \Phi_1, \Phi_2, F_1, F_2 \) are fundamental matrix solutions. The fundamental matrices correspond to
coefficients of the homogeneous solutions $\varphi_h(x)$ and $f_h(x)$ given by
\begin{align}
\varphi_h(x) &= \Phi_1(x)\varphi_j + \Phi_2(x)\varphi_{j+1}, \tag{C.0.6a} \\
f_h(x) &= F_1(x)\varphi_j + F_2(x)\varphi_{j+1}. \tag{C.0.6b}
\end{align}

Now that the system BVP has been rewritten we will first derive the homogeneous flux in section C.1 and derive the inhomogeneous flux in section C.2.

### C.1 Homogeneous flux

For the homogeneous flux $F_h^{j+1/2}$ we only consider the homogeneous ODE system
\begin{align}
q' &= Aq, \tag{C.1.1a} \\
B_{L}q(x_j) + B_{R}q(x_{j+1}) &= \begin{pmatrix} \varphi_j \\ \varphi_{j+1} \end{pmatrix} = r. \tag{C.1.1b}
\end{align}

The general homogeneous solution to this ODE system is given by
\begin{align}
q_h(x) &= e^{Ax}p. \tag{C.1.2}
\end{align}

where $p$ is a vector to be determined from the boundary conditions. Thus upon applying the boundary conditions we find
\begin{align}
B_{L}e^{Ax_j}p + B_{R}e^{Ax_{j+1}}p &= \begin{pmatrix} \varphi_j \\ \varphi_{j+1} \end{pmatrix} = r. \tag{C.1.3}
\end{align}

Assume now that the matrix $A$ has a complete set of eigenvectors $v_k$ with eigenvalues $\lambda_k$ (for $k = 1, ..., 2m$), then the spectral decomposition of the matrix $A$ is given by
\begin{align}
A = V\Lambda V^{-1}, \quad V = (v_1, ..., v_{2m}), \quad \Lambda = \text{diag} (\lambda_1, ..., \lambda_{2m}). \tag{C.1.4}
\end{align}

The matrices $V$ and $\Lambda$ will be partitioned into submatrices of size $m \times m$, according to
\begin{align}
V &= \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}, \\
\Lambda &= \begin{pmatrix} \Lambda_1 & 0 \\ 0 & \Lambda_2 \end{pmatrix},
\end{align}

with $\Lambda_1 = \text{diag} (\lambda_1, ..., \lambda_m)$ and $\Lambda_2 = \text{diag} (\lambda_{m+1}, ..., \lambda_{2m})$. Therefore relation \(C.1.3\) can be rewritten to
\begin{align}
r &= \begin{pmatrix} V_{11} & V_{12} \\ 0 & 0 \end{pmatrix} \begin{pmatrix} e^{\Lambda_1 x_j} & 0 \\ 0 & e^{\Lambda_2 x_j} \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ V_{11} & V_{12} \end{pmatrix} \begin{pmatrix} e^{\Lambda_1 x_{j+1}} & 0 \\ 0 & e^{\Lambda_2 x_{j+1}} \end{pmatrix} V^{-1}p \tag{C.1.5} \\
= \begin{pmatrix} V_{11}e^{\Lambda_1 x_j} & V_{12}e^{\Lambda_2 x_j} \\ V_{11}e^{\Lambda_1 x_{j+1}} & V_{12}e^{\Lambda_2 x_{j+1}} \end{pmatrix} V^{-1}p, \tag{C.1.6}
\end{align}

thus the vector $p$ is given by
\begin{align}
p = V \begin{pmatrix} V_{11}e^{\Lambda_1 x_j} & V_{12}e^{\Lambda_2 x_j} \\ V_{11}e^{\Lambda_1 x_{j+1}} & V_{12}e^{\Lambda_2 x_{j+1}} \end{pmatrix}^{-1} r. \tag{C.1.7}
\end{align}

In order to improve readability we introduce the block matrix $T$ defined by
\begin{align}
T := \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} = \begin{pmatrix} V_{11}e^{\Lambda_1 x_j} & V_{12}e^{\Lambda_2 x_j} \\ V_{11}e^{\Lambda_1 x_{j+1}} & V_{12}e^{\Lambda_2 x_{j+1}} \end{pmatrix}^{-1}. \tag{C.1.8}
\end{align}
The submatrices of $T$ can be found by using the block matrix inversion given by equation (B.1.3). In the block matrix inversion it is assumed that each submatrix of $T^{-1}$ is invertible. This is no real restriction since we will require the submatrices $V_{11}$ and $V_{12}$ to be regular in the final result and the other matrices involving the matrix exponential are obviously regular. The matrix inversion results in

\[
\begin{align*}
T_{11} &= (V_{11}e^{\Lambda_{1}x_{j}} - V_{12}e^{-\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}x_{j+1}})^{-1}, \\
T_{12} &= (V_{11}e^{\Lambda_{1}x_{j+1}} - V_{12}e^{\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}x_{j}})^{-1}, \\
T_{21} &= (V_{12}e^{\Lambda_{2}x_{j}} - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}x_{j+1}})^{-1}, \\
T_{22} &= (V_{12}e^{\Lambda_{2}x_{j+1}} - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}x_{j}})^{-1}.
\end{align*}
\]

The general solution $q(x)$ is thus given by

\[
\begin{align*}
q^h(x) &= (\varphi^h(x))f^h(x) = e^{\Lambda x}p \\
&= Ve^{\Lambda x}V^{-1}p \\
&= Ve^{\Lambda x}Tr \\
&= \left(\begin{array}{ccc}
V_{11} & V_{12} \\
V_{21} & V_{22}
\end{array}\right) \left(\begin{array}{ccc}
0 & e^{\Lambda x} & 0 \\
0 & 0 & e^{\Lambda x}
\end{array}\right) \left(\begin{array}{ccc}
T_{11} & T_{12} \\
T_{21} & T_{22}
\end{array}\right) \left(\begin{array}{c}
\varphi_j \\
\varphi_{j+1}
\end{array}\right)
\]
\]

\[
\begin{align*}
&= \left(\begin{array}{ccc}
V_{11}e^{\Lambda_{1}x_{j}} & V_{12}e^{\Lambda_{2}\Delta x} \\
V_{21}e^{\Lambda_{1}x_{j}} & V_{22}e^{\Lambda_{2}\Delta x}
\end{array}\right) \left(\begin{array}{ccc}
T_{11} & T_{12} \\
T_{21} & T_{22}
\end{array}\right) \left(\begin{array}{c}
\varphi_j \\
\varphi_{j+1}
\end{array}\right)
\end{align*}
\]

\[
\begin{align*}
&= \left(\begin{array}{c}
\Phi_1 \\
\Phi_2
\end{array}\right) \left(\begin{array}{c}
\varphi_j \\
\varphi_{j+1}
\end{array}\right),
\end{align*}
\]

where in the last step we defined the fundamental matrix solutions $\Phi_1, \Phi_2, F_1, F_2$. Next we introduce the scaled coordinate $\sigma(x) = (x - x_j)/\Delta x$ and find expressions for the matrix solutions

\[
\begin{align*}
\Phi_1(x) &= V_{11}e^{\Lambda_{1}x}T_{11} + V_{12}e^{\Lambda_{2}\Delta x}T_{21} \\
&= V_{11}e^{\Lambda_{1}x}(V_{11}e^{\Lambda_{1}x_{j}} - V_{12}e^{-\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}x_{j+1}})^{-1} \\
&\quad + V_{12}e^{\Lambda_{2}\Delta x}(V_{12}e^{\Lambda_{2}x_{j}} - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}x_{j+1}})^{-1} \\
&= V_{11}e^{\Lambda_{1}x}(V_{11} - V_{12}e^{-\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}\Delta x}e^{\Lambda_{1}x_{j}})^{-1} \\
&\quad + V_{12}e^{\Lambda_{2}\Delta x}(V_{12} - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}\Delta x}e^{\Lambda_{2}x_{j}})^{-1} \\
&= V_{11}e^{\Lambda_{1}x(x-x_j)}(V_{11} - V_{12}e^{-\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}\Delta x})^{-1} \\
&\quad + V_{12}e^{\Lambda_{2}\Delta x(x-x_j)}(V_{12} - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}\Delta x})^{-1} \\
&= V_{11}e^{\Lambda_{1}\Delta x}\sigma(x-x_j)(I - V_{12}e^{-\Lambda_{2}\Delta x}V_{12}^{-1}V_{11}e^{\Lambda_{1}\Delta x}V_{11}^{-1})^{-1} \\
&\quad + V_{12}e^{\Lambda_{2}\Delta x}\sigma(x-x_j)(I - V_{11}e^{-\Lambda_{1}\Delta x}V_{11}^{-1}V_{12}e^{\Lambda_{2}\Delta x}V_{12}^{-1})^{-1}.
\end{align*}
\]
\[ F_1(x) = V_{21}e^{A_1 x}T_{11} + V_{22}e^{A_2 x}T_{21} \]
\[ = V_{21}e^{A_1 x} \left( V_{11}e^{A_1 x_j} - V_{12}e^{-A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 x_j+i} \right)^{-1} \]
\[ + V_{22}e^{A_2 x} \left( V_{12}e^{A_2 x_j} - V_{11}e^{-A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 x_j+i} \right)^{-1} \]
\[ = V_{21}e^{A_1 x} \left( \left( V_{11} - V_{12}e^{-A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 x_j} \right)e^{A_1 x_j} \right)^{-1} \]
\[ + V_{22}e^{A_2 x} \left( \left( V_{12} - V_{11}e^{-A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 \Delta x} \right)e^{A_2 x_j} \right)^{-1} \]
\[ = V_{21}e^{A_1 (x-x_j)} \left( V_{11} - V_{12}e^{-A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 \Delta x} \right)^{-1} \]
\[ + V_{22}e^{A_2 (x-x_j)} \left( V_{12} - V_{11}e^{-A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 \Delta x} \right)^{-1} \]
\[ = V_{21}e^{A_1 \Delta x \sigma} \left( V_{11} - V_{12}e^{-A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 \Delta x} \right)^{-1} \]
\[ + V_{22}e^{A_2 \Delta x \sigma} \left( V_{12} - V_{11}e^{-A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 \Delta x} \right)^{-1} \]
\[ = V_{21}e^{A_1 \Delta x}V_{11}^{-1} \left( I - V_{12}e^{-A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 \Delta x}V_{11}^{-1} \right)^{-1} \]
\[ + V_{22}e^{A_2 \Delta x}V_{12}^{-1} \left( I - V_{11}e^{-A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 \Delta x}V_{12}^{-1} \right)^{-1} , \]

\[ \Phi_2(x) = V_{11}e^{A_1 x}T_{12} + V_{12}e^{A_2 x}T_{22} \]
\[ = V_{11}e^{A_1 x} \left( V_{11}e^{A_1 x_{j+1}} - V_{12}e^{A_2 \Delta x}V_{12}^{-1}V_{11}e^{A_1 x_j} \right)^{-1} \]
\[ + V_{12}e^{A_2 x} \left( V_{12}e^{A_2 x_{j+1}} - V_{11}e^{A_1 \Delta x}V_{11}^{-1}V_{12}e^{A_2 x_j} \right)^{-1} \]
\[ = V_{11}e^{A_1 x} \left( \left( V_{11}e^{A_1 \Delta x} - V_{12}e^{A_2 \Delta x}V_{12}^{-1}V_{11} \right)e^{A_1 x_j} \right)^{-1} \]
\[ + V_{12}e^{A_2 x} \left( \left( V_{12}e^{A_2 \Delta x} - V_{11}e^{A_1 \Delta x}V_{11}^{-1}V_{12} \right)e^{A_2 x_j} \right)^{-1} \]
\[ = V_{11}e^{A_1 (x-x_j)} \left( V_{11}e^{A_1 \Delta x} - V_{12}e^{A_2 \Delta x}V_{12}^{-1}V_{11} \right)^{-1} \]
\[ + V_{12}e^{A_2 (x-x_j)} \left( V_{12}e^{A_2 \Delta x} - V_{11}e^{A_1 \Delta x}V_{11}^{-1}V_{12} \right)^{-1} \]
\[ = V_{11}e^{A_1 \Delta x \sigma} \left( V_{11}e^{A_1 \Delta x} - V_{12}e^{A_2 \Delta x}V_{12}^{-1}V_{11} \right)^{-1} \]
\[ + V_{12}e^{A_2 \Delta x \sigma} \left( V_{12}e^{A_2 \Delta x} - V_{11}e^{A_1 \Delta x}V_{11}^{-1}V_{12} \right)^{-1} \]
\[ = V_{11}e^{-A_1 \Delta x (1-\sigma)}V_{11}^{-1} \left( I - V_{12}e^{A_2 \Delta x}V_{12}^{-1}V_{11}e^{-A_1 \Delta x}V_{11}^{-1} \right)^{-1} \]
\[ + V_{12}e^{-A_2 \Delta x (1-\sigma)}V_{12}^{-1} \left( I - V_{11}e^{A_1 \Delta x}V_{11}^{-1}V_{12}e^{-A_2 \Delta x}V_{12}^{-1} \right)^{-1} . \]
\[ F_2(x) = V_{12}e^{Ax} T_{12} + V_{22}e^{Ax} T_{22} \]
\[ = V_{12}e^{Ax} (V_{11}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11}e^{Ax} x_j)^{-1} \]
\[ + V_{22}e^{Ax} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{12}e^{Ax} x_j)^{-1} \]
\[ = V_{12}e^{Ax} ((V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11}) e^{Ax} x_j)^{-1} \]
\[ + V_{22}e^{Ax} ((V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11}) e^{Ax} x_j)^{-1} \]
\[ = V_{12}e^{Ax} x_{j-1} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]
\[ = V_{12}e^{Ax} x_{j} (V_{11}e^{Ax} x_j - V_{12}e^{Ax} x_{j+1} V_{11})^{-1} \]
\[ + V_{22}e^{Ax} x_{j+1} (V_{12}e^{Ax} x_{j+1} - V_{12}e^{Ax} x_{j} V_{12}^{-1} V_{11})^{-1} \]

These fundamental matrix solutions can be rewritten by defining the matrices $B_1$ and $B_2$ as
\[ B_1 := V_{11}A_1 V_{11}^{-1}, \]
\[ B_2 := V_{12}A_2 V_{12}^{-1}, \]
where both matrices are defined by an eigendecomposition. Therefore applying the function $g(z)$ on the matrix $B_1$ results in $g(B_1) = V_{11}g(A_1) V_{11}^{-1} = V_{11} \text{diag} (g(\lambda_1), ..., g(\lambda_m)) V_{11}^{-1}$. For $B_2$ obviously a similar result holds. Now the fundamental matrix solutions can be rewritten to
\[ \Phi_1(x) = e^{B_1 x} (I - e^{-B_2 x} e^{B_1 x})^{-1} + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1}, \]
\[ \Phi_2(x) = e^{-B_1 x} (I - e^{-B_2 x} e^{B_1 x})^{-1} + e^{-B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1}, \]
\[ F_1(x) = V_{12}V_{11} e^{B_1 x} (I - e^{-B_2 x} e^{B_1 x})^{-1} \]
\[ + V_{22}V_{12} e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1}, \]
\[ F_2(x) = V_{21}V_{11} e^{-B_1 x} (I - e^{-B_2 x} e^{B_1 x})^{-1} \]
\[ + V_{22}V_{12} e^{-B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1}. \]

We now manipulate the fundamental matrix solutions into more usable expressions. For the fluxes we additionally use the definition of the fundamental matrix flux $F_i := U \Phi_i - \mathcal{E} \Phi_i$ for $i = 1,2$ to obtain the following relations
\[ U - \mathcal{E} B_1 = V_{21} V_{11}^{-1} \]
\[ U - \mathcal{E} B_2 = V_{22} V_{12}^{-1} \]
For $\Phi_1$ we find
\[ \Phi_1(x) = e^{B_1 x} (I - e^{-B_2 x} e^{B_1 x})^{-1} + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1} \]
\[ = e^{B_1 x} (e^{-B_1 x} e^{B_2 x}) (e^{-B_1 x} e^{B_2 x})^{-1} \]
\[ + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1} \]
\[ = e^{B_1 x} (e^{B_2 x} (I - e^{B_1 x} e^{B_2 x})^{-1} + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1} \]
\[ = (e^{B_2 x} (I - e^{B_1 x} e^{B_2 x})^{-1} + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1} \]
\[ = \left( e^{B_2 x} (I - e^{B_1 x} e^{B_2 x})^{-1} + e^{B_2 x} (I - e^{-B_1 x} e^{B_2 x})^{-1} \right). \]
For $\Phi_2$ we find

$$
\Phi_2(x) = e^{-B_1x(1-\sigma)} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} + e^{-B_2x}(1-\sigma) \left( I - e^{B_1x} e^{-B_2x} \right)^{-1}
$$

$$
= e^{-B_1x(1-\sigma)} \left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ e^{-B_2x}(1-\sigma) \left( I - e^{B_1x} e^{-B_2x} \right)^{-1}
$$

$$
= e^{B_1x}\left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} + e^{B_2x}(1-\sigma) \left( I - e^{B_1x} e^{-B_2x} \right)^{-1}
$$

$$
= (e^{B_2x} - e^{B_1x}) \left( e^{B_2x} - e^{B_1x} \right)^{-1}.
$$

For $F_1$ we find

$$
F_1(x) = V_21 V_1^{-1} e^{B_1x} \left( I - e^{B_2x} e^{-B_2x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= V_21 V_1^{-1} e^{B_1x} \left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= V_21 V_1^{-1} e^{B_1x} \left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= \left( V_22 V_1^{-1} e^{B_1x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right)
$$

$$
= \left( U - \mathcal{E}B_1 \right) e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= \left( U \left( e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right) - \mathcal{E} \left( B_2 e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right) \right)
$$

$$
= \left( e^{B_2x} - e^{B_1x} \right)^{-1}.
$$

For $F_2$ we find

$$
F_2(x) = V_21 V_1^{-1} e^{B_1x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= V_21 V_1^{-1} e^{B_1x} \left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= V_21 V_1^{-1} e^{B_1x} \left( e^{B_1x} e^{-B_2x} \right) \left( e^{B_1x} e^{-B_1x} \right)^{-1} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
+ V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= \left( V_22 V_1^{-1} e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right)
$$

$$
= \left( U - \mathcal{E}B_2 \right) e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1}
$$

$$
= \left( U \left( e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right) - \mathcal{E} \left( B_2 e^{B_2x} \left( I - e^{B_1x} e^{-B_1x} \right)^{-1} \right) \right)
$$

$$
= \left( e^{B_2x} - e^{B_1x} \right)^{-1}.
$$

The homogeneous flux $F_{j+1/2}^h$ is given by $F(x_{j+1/2}) = F_1(x_{j+1/2})\varphi_j + F_2(x_{j+1/2})\varphi_{j+1}$, thus we find

$$
F_1(x_{j+1/2}) = \left[ U \left( e^{B_2x/2} - e^{B_1x/2} \right) - \mathcal{E} \left( B_2 e^{B_2x/2} - B_1 e^{B_1x/2} \right) \right]
$$

$$
\left( e^{B_2x} - e^{B_1x} \right)^{-1},
$$

(C.1.13a)

$$
F_2(x_{j+1/2}) = \left[ U \left( e^{B_2x/2} - e^{B_1x/2} \right) - \mathcal{E} \left( B_2 e^{B_2x/2} - B_1 e^{B_1x/2} \right) \right]
$$

$$
\left( e^{B_2x} - e^{B_1x} \right)^{-1}.
$$

(C.1.13b)
C.2 Inhomogeneous flux

For the inhomogeneous flux $F_{j+1/2}$ we use the homogeneous fundamental matrix solution $Q$ derived in the previous section and apply variation of constants. The ODE system is given by

$$q' = Aq + b. \quad (C.2.1)$$

Now we apply variation of constants such that

$$q(x) = Q(x)\alpha(x), \quad (C.2.2)$$

therefore $q' = Q'\alpha + Q\alpha' = AQ\alpha + b$ which implies $\alpha'(x) = Q^{-1}(x)b(x)$, since $Q' = AQ$. Upon integrating $\alpha'(x)$ from $x_j$ to $x$ we find

$$\alpha(x) - \alpha(x_j) = \int_{x_j}^{x} Q^{-1}(y)b(y)dy, \quad (C.2.3)$$

with $\alpha(x_j)$ a constant vector. Applying boundary conditions for $q(x)$ results in

$$B_LQ(x_j)\alpha(x_j) + B_RQ(x_{j+1})\left(\alpha(x_j) + \int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy\right) = r, \quad (C.2.4)$$

therefore

$$\alpha(x_j) = r - B_RQ(x_{j+1})\int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy. \quad (C.2.5)$$

Using this we can obtain the solution $q(x)$

$$q(x) = Q(x)r - Q(x)B_RQ(x_{j+1})\int_{x_j}^{x_{j+1}} Q^{-1}(y)b(y)dy + Q(x)\int_{x_j}^{x} Q^{-1}(y)b(y)dy, \quad (C.2.6)$$

which can be rewritten to

$$q(x) = q^h(x) + \int_{x_j}^{x_{j+1}} G(x;y)b(y)dy, \quad (C.2.7a)$$

$$q^h(x) := Q(x)r. \quad (C.2.7b)$$

Using the boundary conditions for $Q(x)$ we find the Green’s function $G(x;y)$

$$G(x;y) = \begin{cases} G_L(x;y) \\ G_R(x;y) \end{cases} = \begin{cases} Q(x)B_LQ(x_j)Q^{-1}(y) \\ -Q(x)B_RQ(x_{j+1})Q^{-1}(y) \end{cases} \quad \text{for } x_j < y < x, \quad (C.2.8)$$

The Green’s function can be partitioned according to

$$G(x;y) = \begin{cases} (G_{L,11} G_{L,12}) \\ (G_{L,21} G_{L,22}) \end{cases} \quad \text{for } x_j < y < x, \quad (C.2.9)$$

$$\begin{cases} (G_{R,11} G_{R,12}) \\ (G_{R,21} G_{R,22}) \end{cases} \quad \text{for } x < y < x_{j+1},$$

where the submatrices of $G_L, G_R$ are of size $m \times m$. Note that

$$B_LQ(x_j) = \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix}, \quad B_RQ(x_{j+1}) = \begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix},$$
therefore only certain components of $Q^{-1}$ are needed. In order to find $G_L(x; y)$ and $G_R(x; y)$ we use again the block matrix inverse given by equation (B.1.3), resulting in

\[
G_L(x; y) = \begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}(x) \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix} \left( \begin{pmatrix} \Phi_1 - \Phi_2 F_2^{-1} F_1 \\ F_1 - F_2 \Phi_2^{-1} \Phi_1 \end{pmatrix} \right)^{-1}(y)
\]

\[
= \begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}(x) \left( \begin{pmatrix} \Phi_1 - \Phi_2 F_2^{-1} F_1 \\ F_1 - F_2 \Phi_2^{-1} \Phi_1 \end{pmatrix} \right)^{-1}(y), \quad (C.2.10)
\]

\[
G_R(x; y) = -\begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}(x) \begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix} \left( \begin{pmatrix} \Phi_2 - \Phi_1 F_1^{-1} F_2 \\ F_2 - \Phi_1 F_1^{-1} \Phi_2 \end{pmatrix} \right)^{-1}(y)
\]

\[
= -\begin{pmatrix} \Phi_1 & \Phi_2 \\ F_1 & F_2 \end{pmatrix}(x) \left( \begin{pmatrix} \Phi_2 - \Phi_1 F_1^{-1} F_2 \\ F_2 - \Phi_1 F_1^{-1} \Phi_2 \end{pmatrix} \right)^{-1}(y). \quad (C.2.11)
\]

The flux only requires the submatrices $G_{L,22}$ and $G_{R,22}$, for which we find

\[
G_{L,22}(x; y) = F_1(x) \left( F_1 - F_2 \Phi_2^{-1} \Phi_1 \right)^{-1}(y), \quad (C.2.12a)
\]

\[
G_{R,22}(x; y) = -F_2(x) \left( F_2 - \Phi_1 \Phi_2^{-1} \Phi_2 \right)^{-1}(y). \quad (C.2.12b)
\]

The Green’s functions can be rewritten using the definition of the flux for matrices

\[
F_i := U \Phi_i - \mathcal{E} \Phi'_i, \quad \text{for } i = 1, 2, \quad (C.2.13)
\]

where the prime $'$ denotes differentiation to the $x$-coordinate. The Green’s functions can be rewritten to

\[
G_{L,22}(x; y) = F_1(x) \left( U \Phi_1 - \mathcal{E} \Phi'_1 - (U \Phi_2 - \mathcal{E} \Phi'_2) \Phi_2^{-1} \Phi_1 \right)^{-1}(y)
\]

\[
= F_1(x) \left( -\mathcal{E} \Phi'_1 + \mathcal{E} \Phi'_2 \Phi_2^{-1} \Phi_1 \right)^{-1}(y)
\]

\[
= F_1(x) \left( \mathcal{E} \left( \Phi_2 \Phi_2^{-1} - \Phi_1 \Phi_1^{-1} \right) \Phi_1 \right)^{-1}(y)
\]

\[
= F_1(x) \Phi_1^{-1}(y) \left( \Phi_2 \Phi_2^{-1} - \Phi_1 \Phi_1^{-1} \right)^{-1}(y) \mathcal{E}^{-1} \quad (C.2.14)
\]

and

\[
G_{R,22}(x; y) = -F_2(x) \left( U \Phi_2 - \mathcal{E} \Phi'_2 - (U \Phi_1 - \mathcal{E} \Phi'_1) \Phi_1^{-1} \Phi_2 \right)^{-1}(y)
\]

\[
= -F_2(x) \left( -\mathcal{E} \Phi'_2 + \mathcal{E} \Phi'_1 \Phi_1^{-1} \Phi_2 \right)^{-1}(y)
\]

\[
= F_2(x) \left( \mathcal{E} \left( \Phi_1 \Phi_2^{-1} - \Phi'_1 \Phi_1^{-1} \right) \Phi_2 \right)^{-1}(y)
\]

\[
= F_2(x) \Phi_2^{-1}(y) \left( \Phi_1 \Phi_2^{-1} - \Phi'_1 \Phi_1^{-1} \right)^{-1}(y) \mathcal{E}^{-1}. \quad (C.2.15)
\]

The numerical flux $F_{j+1/2} = F_{j+1/2}^h + F_{j+1/2}^i$ can then be found from $f(x_{j+1/2})$. Therefore the homogeneous flux $F_{j+1/2}^h$ and inhomogeneous flux $F_{j+1/2}^i$ are then given by

\[
F_{j+1/2}^h = F_1(x_{j+1/2}) \varphi_j + F_2(x_{j+1/2}) \varphi_{j+1}, \quad (C.2.16a)
\]

\[
F_{j+1/2}^i = F_1(x_{j+1/2}) \int_{x_j}^{x_{j+1}} \Phi_1^{-1}(y) \left( \Phi_2 \Phi_2^{-1} - \Phi'_1 \Phi_1^{-1} \right)^{-1}(y) \mathcal{E}^{-1} s(y) dy
\]

\[
+ F_2(x_{j+1/2}) \int_{x_{j+1/2}}^{x_{j+1}} \Phi_2^{-1}(y) \left( \Phi'_2 \Phi_2^{-1} - \Phi'_1 \Phi_1^{-1} \right)^{-1}(y) \mathcal{E}^{-1} s(y) dy. \quad (C.2.16b)
\]

Now define the matrix $W$ by

\[
W := \Phi_2 \Phi_2^{-1} - \Phi'_1 \Phi_1^{-1}. \quad (C.2.17)
\]
C.3. Singularity in numerical solution

Substituting the relations for $\Phi_1$ and $\Phi_2$ we find

$$ W = (B_2 e^{B_2 \Delta x} - B_1 e^{B_1 \Delta x}) (e^{B_2 \Delta x} - e^{B_1 \Delta x})^{-1} $$

\[
- \left( B_2 e^{B_2 \Delta x(1-\sigma)} - B_1 e^{B_1 \Delta x(1-\sigma)} \right) \left( e^{B_2 \Delta x(1-\sigma)} - e^{B_1 \Delta x(1-\sigma)} \right)^{-1}.
\]  

(C.2.18)

Thus using the assumption that the diffusion matrix $\mathcal{E}$ is constant between the nodal points $[x_j, x_{j+1}]$ and in addition assume that the source $s$ is constant over the control volume $[x_{j-1/2}, x_{j+1/2}]$, then the integrals we need to solve are given by

$$ I_1 := \int_{x_j}^{x_{j+1/2}} \Phi_1^{-1}(y) \left( \Phi_2^{-1} \Phi_2^{-1} - \Phi_1^{-1} \Phi_1^{-1} \right)^{-1} (y) dy, $$

(C.2.19a)

$$ I_2 := \int_{x_j}^{x_{j+1}} \Phi_2^{-1}(y) \left( \Phi_2^{-1} \Phi_2^{-1} - \Phi_1^{-1} \Phi_1^{-1} \right)^{-1} (y) dy, $$

(C.2.19b)

with the inhomogeneous flux given by

$$ F^i_{j+1/2} = F_1(x_{j+1/2}) I_1 \mathcal{E}^{-1} s_j + F_2(x_{j+1/2}) I_2 \mathcal{E}^{-1} s_{j+1}. $$

(C.2.19c)

Substituting the expressions for $\Phi_1, \Phi_2$ and $W$, followed by a transformation to the scaled coordinate results into

$$ I_1 = \Delta x \left( e^{B_2 \Delta x} - e^{B_1 \Delta x} \right) \int_0^{1/2} \left( e^{B_2 \Delta x(1-\sigma)} - e^{B_1 \Delta x(1-\sigma)} \right)^{-1} $$

\[
\cdot \left[ (B_2 e^{B_2 \Delta x} - B_1 e^{B_1 \Delta x}) (e^{B_2 \Delta x} - e^{B_1 \Delta x})^{-1} 
- \left( B_2 e^{B_2 \Delta x(1-\sigma)} - B_1 e^{B_1 \Delta x(1-\sigma)} \right) \left( e^{B_2 \Delta x(1-\sigma)} - e^{B_1 \Delta x(1-\sigma)} \right)^{-1} \right]^{-1} d\sigma,
\]

and

$$ I_2 = \Delta x \left( e^{B_2 \Delta x} - e^{B_1 \Delta x} \right) \int_{1/2}^{1} \left( e^{B_2 \Delta x} - e^{B_1 \Delta x} \right)^{-1} $$

\[
\cdot \left[ (B_2 e^{B_2 \Delta x} - B_1 e^{B_1 \Delta x}) (e^{B_2 \Delta x} - e^{B_1 \Delta x})^{-1} 
- \left( B_2 e^{B_2 \Delta x(1-\sigma)} - B_1 e^{B_1 \Delta x(1-\sigma)} \right) \left( e^{B_2 \Delta x(1-\sigma)} - e^{B_1 \Delta x(1-\sigma)} \right)^{-1} \right]^{-1} d\sigma.
\]

Evaluating these integrals analytically seems rather difficult.

C.3 Singularity in numerical solution

When solving the coupled ADR system using the above equations there can be inverse operations on matrices that might be singular. Consider the following example

$$ \frac{d}{dx} \left( U \varphi - \mathcal{E} \frac{d \varphi}{dx} \right) = C \varphi, $$

(C.3.1)

where the first equation is rewritten to

$$ \frac{d}{dx} \left( P \varphi - \frac{d \varphi}{dx} \right) = D a \varphi, $$

(C.3.2)
with the Péclet matrix $\text{Pe} := \mathcal{E}^{-1}UL$ and the diffusive Damköhler matrix $\text{Da}^d := \mathcal{E}^{-1}CL^2$. In our example $L = 1$, and the diffusion matrix is given by the identity matrix ($\mathcal{E} = I$), and we choose the Péclet and diffusive Damköhler matrices such that they commute, i.e.

$$\text{Pe} := W\Omega W^{-1}, \quad \text{Da}^d := WMW^{-1},$$

where the matrices share the same eigenvectors $W = (w_1, w_2)$, and the matrices $\Omega = \text{diag}(\omega_1, \omega_2)$ and $M = \text{diag}(\mu_1, \mu_2)$ commute. The matrix $A$ is then given by

$$A = \begin{pmatrix} \omega_1 & 0 & -1 & 0 \\ 0 & \omega_2 & 0 & -1 \\ \mu_1 & 0 & 0 & 0 \\ 0 & \mu_2 & 0 & 0 \end{pmatrix}.$$  \hspace{1cm} (C.3.4)

The eigendecomposition of $A$ is given by $A = V\Lambda V^{-1}$ where

$$\Lambda = \text{diag} \left( \frac{1}{2} \omega_1(1 + r_1), \frac{1}{2} \omega_1(1 - r_1), \frac{1}{2} \omega_2(1 + r_2), \frac{1}{2} \omega_2(1 - r_2) \right), \quad \text{and} \quad V = \begin{pmatrix} \frac{1}{2} \mu_1(1 + r_1) & \frac{1}{2} \mu_1(1 - r_1) & 0 & 0 \\ 0 & 0 & \frac{1}{2} \mu_2(1 + r_2) & \frac{1}{2} \mu_2(1 - r_2) \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{pmatrix},$$

where $r_i = \sqrt{1 - 4\mu_i/\omega_i^2}$. If we now use the partitioning of the eigenvector matrix $V$ we find

$$V_{11} = \begin{pmatrix} \frac{1}{2} \mu_1(1 + r_1) & \frac{1}{2} \mu_1(1 - r_1) & 0 & 0 \\ 0 & 0 & \frac{1}{2} \mu_2(1 + r_2) & \frac{1}{2} \mu_2(1 - r_2) \end{pmatrix},$$

$$V_{12} = \begin{pmatrix} \frac{1}{2} \mu_1(1 + r_1) & \frac{1}{2} \mu_1(1 - r_1) & 0 & 0 \\ 0 & 0 & \frac{1}{2} \mu_2(1 + r_2) & \frac{1}{2} \mu_2(1 - r_2) \end{pmatrix},$$

for which both submatrices are singular. However it is still possible to obtain a solution by simply switching the 2nd and 3rd eigenvalue in $\Lambda$ and corresponding eigenvectors in $V$, then the submatrices will be regular (assuming that $r_i \neq 1$):

$$\Lambda = \text{diag} \left( \frac{1}{2} \omega_1(1 + r_1), \frac{1}{2} \omega_2(1 + r_2), \frac{1}{2} \omega_1(1 - r_1), \frac{1}{2} \omega_2(1 - r_2) \right), \quad \text{and} \quad V_{11} = \begin{pmatrix} \frac{1}{2} \mu_1(1 + r_1) & 0 & \frac{1}{2} \mu_2(1 + r_2) & 0 \\ 0 & \frac{1}{2} \mu_2(1 + r_2) & 0 & \frac{1}{2} \mu_2(1 + r_2) \end{pmatrix},$$

$$V_{12} = \begin{pmatrix} \frac{1}{2} \mu_1(1 - r_1) & 0 & \frac{1}{2} \mu_2(1 - r_2) & 0 \\ 0 & \frac{1}{2} \mu_2(1 - r_2) & 0 & \frac{1}{2} \mu_2(1 - r_2) \end{pmatrix}. \quad \text{(C.3.6c)}$$

### C.4 Verifying the fundamental matrix solutions

Since $F_i := U\Phi_i - \mathcal{E}\Phi_i^t$ for $i = 1, 2$ it follows that

$$U - \mathcal{E}B_1 = V_{21}V_{11}^{-1} \Leftrightarrow UV_{11} - \mathcal{E}V_{11}A_1 = V_{21},$$

$$U - \mathcal{E}B_2 = V_{22}V_{12}^{-1} \Leftrightarrow UV_{12} - \mathcal{E}V_{12}A_2 = V_{22}. $$

In order to verify the fundamental solutions we substitute the solution $\varphi(x)$ in the homogeneous ADR problem given by equation (C.0.1a) with $s(\varphi) = 0$. From $\varphi(x) = \Phi_1(x)\varphi_j + \Phi_2(x)\varphi_{j+1}$ we
find that
\[
\frac{d}{dx} \left( U\Phi_1 - \mathcal{E} \frac{d\Phi_1}{dx} \right) - C\Phi_1 = 0, \\
\frac{d}{dx} \left( U\Phi_2 - \mathcal{E} \frac{d\Phi_2}{dx} \right) - C\Phi_2 = 0,
\] (C.4.1a)
(C.4.1b)

must hold for the obtained \( \Phi_1(x) \) and \( \Phi_2(x) \). This implies that
\[
\frac{d}{dx} \left( U\Phi_1 - \mathcal{E} \frac{d\Phi_1}{dx} \right) - C\Phi_1 = (UB_1 - \mathcal{E}B_1^2 - C)e^{B_1 \Delta x} \left( I - e^{-B_1 \Delta x}e^{B_1 \Delta x} \right)^{-1} \\
\quad + (UB_2 - \mathcal{E}B_2^2 - C)e^{B_2 \Delta x} \left( I - e^{-B_1 \Delta x}e^{B_1 \Delta x} \right)^{-1},
\]
\[
\frac{d}{dx} \left( U\Phi_2 - \mathcal{E} \frac{d\Phi_2}{dx} \right) - C\Phi_2 = (UB_1 - \mathcal{E}B_1^2 - C)e^{-B_1 \Delta x(1-\sigma)} \left( I - e^{B_2 \Delta x}e^{-B_1 \Delta x} \right)^{-1} \\
\quad + (UB_2 - \mathcal{E}B_2^2 - C)e^{-B_2 \Delta x(1-\sigma)} \left( I - e^{B_1 \Delta x}e^{-B_2 \Delta x} \right)^{-1}.
\]
The expressions can be reduced using
\[
UB_1 - \mathcal{E}B_1^2 - C = UV_{11}\Lambda_1 V_{11}^{-1} - \mathcal{E}V_{11}\Lambda_1^2 V_{11}^{-1} - C \\
= -\mathcal{E} \left( -\mathcal{E}^{-1}UV_{11}\Lambda_1 + V_{11}\Lambda_1^2 + \mathcal{E}^{-1}CV_{11} \right) V_{11}^{-1} \\
= -\mathcal{E} \left( V_{11}\Lambda_1^2 - \mathcal{E}^{-1}UV_{11}\Lambda_1 + \mathcal{E}^{-1}CV_{11} \right) V_{11}^{-1},
\] (C.4.2a)
\[
UB_2 - \mathcal{E}B_2^2 - C = UV_{12}\Lambda_2 V_{12}^{-1} - \mathcal{E}V_{12}\Lambda_2^2 V_{12}^{-1} - C \\
= -\mathcal{E} \left( -\mathcal{E}^{-1}UV_{12}\Lambda_2 + V_{12}\Lambda_2^2 + \mathcal{E}^{-1}CV_{12} \right) V_{12}^{-1} \\
= -\mathcal{E} \left( V_{12}\Lambda_2^2 - \mathcal{E}^{-1}UV_{12}\Lambda_2 + \mathcal{E}^{-1}CV_{12} \right) V_{12}^{-1}.
\] (C.4.2b)

In the equations (C.4.2a) - (C.4.2b) there is a coefficient matrix related to the generalized eigenvalue problem. This can be made clear by using \( V_{11} = (v_{1,11},...,v_{m,11}) \), \( V_{12} = (v_{1,12},...,v_{m,12}) \), \( \Lambda_1 = \text{diag}(\lambda_1,...,\lambda_m) \) and \( \Lambda_2 = \text{diag}(\lambda_{m+1},...,\lambda_{2m}) \)
\[
V_{11}\Lambda_1^2 - \mathcal{E}^{-1}UV_{11}\Lambda_1 + \mathcal{E}^{-1}CV_{11} \Leftrightarrow \\
(\lambda_1^2 v_{1,11}) - \mathcal{E}^{-1}U(\lambda_1 v_{1,11}) + \mathcal{E}^{-1}C(v_{1,11}) = (\lambda_1^2 I - \lambda_1 \mathcal{E}^{-1}U + \mathcal{E}^{-1}C) v_{1,11} = 0, \\
V_{12}\Lambda_2^2 - \mathcal{E}^{-1}UV_{12}\Lambda_2 + \mathcal{E}^{-1}CV_{12} \Leftrightarrow \\
(\lambda_2^2 v_{1,12}) - \mathcal{E}^{-1}U(\lambda_2 v_{1,12}) + \mathcal{E}^{-1}C(v_{1,12}) = (\lambda_2^2 I - \lambda_2 \mathcal{E}^{-1}U + \mathcal{E}^{-1}C) v_{1,12} = 0,
\]
where in the last step we use the fact that for an eigenvalue \( \lambda \) and eigenvector \( v \) pair the following equation holds
\[
(A - \lambda I) v = 0 \\
\begin{pmatrix}
\mathcal{E}^{-1}U - \lambda I & -\mathcal{E}^{-1} \\
-\mathcal{E}^{-1} & -\lambda I
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2
\end{pmatrix} = 0,
\]
where the partitioning of the eigenvector \( v = (v_1, v_2)^T \) has been used. The above eigenvector equation implies
\[
(\mathcal{E}^{-1}U - \lambda I) v_1 - \mathcal{E}^{-1}v_2 = 0, \quad C v_1 - \lambda v_2 = 0, \\
\Leftrightarrow (\lambda^2 I - \lambda \mathcal{E}^{-1}U + \mathcal{E}^{-1}C) v_1 = 0.
\]

To further verify the fundamental solutions \( \Phi_1(x) \) and \( \Phi_2(x) \) we can also apply the boundary conditions, for which the following relations should hold
\[
\Phi_1(x_j) = I, \quad \Phi_2(x_j) = 0, \\
\Phi_1(x_{j+1}) = 0, \quad \Phi_2(x_{j+1}) = I.
\] (C.4.3)
Using the boundary conditions for $\Phi_1(x)$ we find
\[
\Phi_1(x_j) = (e^{-B_2\Delta x} - e^{-B_1\Delta x}) (e^{-B_2\Delta x} - e^{-B_1\Delta x})^{-1} = I,
\]
\[
\Phi_1(x_{j+1}) = (e^{-B_2\Delta x_0} - e^{-B_1\Delta x_0}) (e^{-B_2\Delta x} - e^{-B_1\Delta x})^{-1} = 0.
\]
Using the boundary conditions for $\Phi_2(x)$ we find
\[
\Phi_2(x_j) = (e^{B_2\Delta x_0} - e^{B_1\Delta x_0}) (e^{B_2\Delta x} - e^{B_1\Delta x})^{-1} = 0,
\]
\[
\Phi_2(x_{j+1}) = (e^{B_2\Delta x} - e^{B_1\Delta x}) (e^{B_2\Delta x} - e^{B_1\Delta x})^{-1} = I.
\]

### C.5 Inhomogeneous flux: special case

Note that for the coupled advection-diffusion system and diffusion-reaction system the fundamental matrices $\Phi_1$ and $\Phi'_1$ commute. Therefore the inhomogeneous flux can be rewritten to
\[
G_{1,22}(x; y) = F_1(x) \left( \Phi'_2 \Phi_2^{-1} \Phi_1 - \Phi'_1 \right)^{-1} (y) \mathcal{E}^{-1}
\]
\[
= F_1(x) \left( \Phi_2^{-1} \left( \Phi'_2 \Phi_1 - \Phi'_2 \Phi_1' \right) \right)^{-1} (y) \mathcal{E}^{-1}
\]
\[
= F_1(x) \left( \Phi'_2 \Phi_1 - \Phi'_2 \Phi_1' \right)^{-1} (y) \Phi_2(y) \mathcal{E}^{-1}, \tag{C.5.1}
\]
and if $\Phi_1$ and $\Phi'_1$ commute then
\[
G_{2,22}(x; y) = F_2(x) \left( \Phi'_2 - \Phi'_1 \Phi_1^{-1} \Phi_2 \right)^{-1} (y) \mathcal{E}^{-1}
\]
\[
= F_2(x) \left( \Phi_2^{-1} \left( \Phi_1 \Phi'_2 - \Phi'_2 \Phi_2 \right) \right)^{-1} (y) \mathcal{E}^{-1}
\]
\[
= F_2(x) \left( \Phi_1 \Phi'_2 - \Phi'_2 \Phi_2 \right)^{-1} (y) \Phi_1(y) \mathcal{E}^{-1}. \tag{C.5.2}
\]

The homogeneous flux $F^h_{j+1/2}$ and inhomogeneous flux $F^i_{j+1/2}$ can then be rewritten to
\[
F^h_{j+1/2} = F_1(x_{j+1/2}) \varphi_j + F_2(x_{j+1/2}) \varphi_{j+1}, \tag{C.5.3a}
\]
\[
F^i_{j+1/2} = F_1(x_{j+1/2}) \int_{x_j}^{x_{j+1/2}} \left( \Phi'_2 \Phi_1 - \Phi'_2 \Phi_1' \right)^{-1} (y) \Phi_2(y) \mathcal{E}^{-1} s(y) dy
\]
\[
+ F_2(x_{j+1/2}) \int_{x_{j+1/2}}^{x_{j+1}} \left( \Phi'_2 \Phi_1 - \Phi'_2 \Phi_1' \right)^{-1} (y) \Phi_1(y) \mathcal{E}^{-1} s(y) dy. \tag{C.5.3b}
\]

The above relations are reminiscent of the scalar inhomogeneous flux.
References


