

Computational Methods for Kinetic Reaction Systems

by

Bruce G. Shapiro

A Dissertation Presented in Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Approved April 2020 by the
Graduate Supervisory Committee:

Christian Ringhofer, Chair
Carl L. Gardner
Zdzislaw Jackiewicz
Rodrigo B. Platte
Dragica Vasileska

ARIZONA STATE UNIVERSITY

May 2020

ABSTRACT

This work is concerned with the study and numerical solution of large reaction diffusion systems with applications to the simulation of degradation effects in solar cells. A discussion of the basics of solar cells including the function of solar cells, the degradation of energy efficiency that happens over time, defects that affect solar cell efficiency and specific defects that can be modeled with a reaction diffusion system are included. Also included is a simple model equation of a solar cell. The basics of stoichiometry theory, how it applies to kinetic reaction systems, and some conservation properties are introduced. A model that considers the migration of defects in addition to the reaction processes is considered. A discussion of asymptotics and how it relates to the numerical simulation of the lifetime of solar cells is included. A reduced solution is considered and a presentation of a numerical comparison of the reduced solution with the full solution on a simple test problem is included. Operator splitting techniques are introduced and discussed. Asymptotically preserving schemes combine asymptotics and operator splitting to use reasonable time steps. A presentation of a realistic example of this study applied to solar cells follows.

TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	v
CHAPTER	
1 INTRODUCTION	1
2 SOLAR CELLS	2
2.1 Function	4
2.2 Defects	8
2.3 Lifetime Tests	10
2.3.1 Pictures	12
2.4 A Simple Model Equation	14
3 STOICHIOMETRY THEORY	18
3.1 Stoichiometry Theory	18
3.1.1 Writing Chemical Equations	18
3.1.2 Balancing Equations	19
3.1.3 Reaction Stoichiometry	21
3.1.4 Percent Yield	22
3.2 Conservation Properties	23
4 DEFECT TRANSPORT MODELS	29
5 ASYMPTOTICS	31
5.1 Basic Approach	32
5.2 The Fundamental Theorem of Linear Algebra	35
5.3 Solving the Fast Equations	36
5.4 Conservation	39
5.5 Numerical Solution of the Reduced Problem	41

CHAPTER	Page
6 NUMERICAL COMPARISON	44
6.1 Numerical Scheme for Reduced Solution	44
6.2 Numerical Scheme for Full Solution	45
6.3 A Spatially Homogeneous Example	45
6.4 A Spatially Inhomogeneous Example	48
7 OPERATOR SPLITTING METHODS	53
7.1 Reasons	53
7.2 Self Consistent Potentials and Gummel's Algorithm	55
7.3 General Convergence Theory for Operator Splitting Methods	58
8 ASYMPTOTICALLY PRESERVING SCHEMES	63
8.1 An Asymptotically Preserving Scheme	64
8.2 AP Applied to the Full Solution	65
8.3 AP Applied to the Reduced Solution	66
8.4 Reduced Equations	69
8.5 A Spatially Homogeneous Example	72
8.6 A Spatially Inhomogeneous Example	74
9 EXAMPLE	77
9.1 Solar Cell	77
9.2 Conclusion	81
REFERENCES	83
APPENDIX	
A A SIMPLE EXAMPLE	86
B GUMMEL'S METHOD	90

LIST OF TABLES

Table		Page
6.1	Parameters Used in Computing and Plotting Figure 6.1.	47
6.2	Parameters Used in Computing and Plotting Figure 6.2.	50
6.3	Parameters Used in Computing and Plotting Figure 6.3.	51
8.1	Parameters Used in Computing and Plotting Figure 8.1.	73
8.2	Parameters Used in Computing and Plotting Figure 8.2.	75
8.3	Parameters Used in Computing and Plotting Figure 8.3.	76
9.1	Parameters Used in Computing and Plotting Figures 9.1, 9.2, and 9.3. .	82

LIST OF FIGURES

Figure	Page
2.1 Solar Spectral Irradiance (Pierret (1996))	4
2.2 A p-n Junction Solar Cell with Resistive Load (Neamen (2012))	5
2.3 Maximum Power Rectangle of the Solar Cell $I - V$ Characteristics.	7
2.4 Defective Solar Panel Near Hayden Library.....	13
2.5 Closeup Showing Front Delamination of Solar Panel.	13
2.6 Electrical and Mechanical Components of PV Modules at ASU Apache Parking Structure.	14
2.7 Electrical Components of PV Modules at ASU Apache Parking Structure.	14
2.8 Solution Using the Forward Euler Method	17
2.9 Solution Using Matrices	17
2.10 Forward Euler Solution in 2-D	17
6.1 Comparison of Full Solution to Reduced Solution (Five Species and Two Reactions).	48
6.2 Case 1 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.	52
6.3 Case 2 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.	52
8.1 Comparison of Full to Reduced Solutions for the AP Scheme with Five Species and Two Reactions.....	74
8.2 Case 1 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.	75
8.3 Case 2 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.	76

Figure	Page
9.1 All of the Species at $t = 1 \times 10^{-5}$ Seconds, Which is After the First Time Step.	80
9.2 All of the Species at $t = 0.5$ Seconds.	80
9.3 All of the Species at $t = 1$ Second.	81

Chapter 1

INTRODUCTION

This work is concerned with the study and numerical solution of large reaction diffusion systems with applications to the simulation of degradation effects in solar cells. Chapter 2 discusses the basics of solar cells. It covers the function of solar cells, the degradation of energy efficiency that happens over time, defects that affect solar cell efficiency and highlights specific defects that can be modeled with a reaction diffusion system. Also included is a simple model equation of a solar cell. Chapter 3 discusses the basics of stoichiometry theory and how it applies to kinetic reaction systems. Chapter 4 introduces a model that considers the migration of defects in addition to the reaction processes. Chapter 5 introduces asymptotics. Asymptotics allows us to compute a reduced solution. We will show a comparison of the reduced solution with the full solution on a simple toy problem in Chapter 6. Chapter 7 covers operator splitting techniques. Operator splitting allows us to compute the transport and reaction parts separately at each time step. Chapter 8 addresses asymptotically preserving methods. Asymptotically preserving schemes allow us to combine asymptotics and operator splitting and take reasonable time steps. Chapter 9 presents a realistic example of this study applied to solar cells.

Chapter 2

SOLAR CELLS

A solar cell is a device that turns light into electricity (Macaulay (1988)). Solar cells are created using semiconductor material. Each solar cell is made up of two different types of semiconductor material brought together to form what is called a p-n junction. A p-n junction is formed when a p-type semiconductor is brought into contact with an n-type semiconductor (Neamen (2012)). The letters p and n stand for positively charged holes and negatively charged electrons respectively. Semiconductor junctions are used in many electronic applications. In the case of a solar cell, the p-n junction is specially engineered to convert photon (light) power into electrical power which is then delivered to a load (e.g. calculator, light, home, power grid, etc.).

Consumer solar cell technology is currently limited to approximately 30 percent quantum efficiency which is defined as the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell (Honsberg and Bowden (2019)). Several factors are used to calculate this efficiency. These factors include the cost of creating the solar cells, the lifetime of the solar cells, and the replacement cost. Research is required in the area of solar cell technology in order to find material that is cost effective, efficient, and long lasting. While with many technologies, computer modeling and calculations can be used to determine the efficacy of the design, currently the only experimental way to determine the longevity of solar cell material is via testing. Solar cells must be produced and put into service. Then we have to measure the electric energy output compared to the photon energy input. These measurements need to be recorded for over 20 years in order to

determine if the solar cells have a sufficient lifetime (see Section 2.3). It is here that computer modeling plays an essential role in the design of solar cells.

In Section 2.1 we look at a simple p-n junction solar cell. First we review how the energy of a photon interacts with semiconductor material.

Quantum mechanically, the energy E of a photon is given by the equation $E = hv$ (Neamen (2012)). Here h is Plank's constant and v is the frequency of the photon (light wave). If we define the wavelength of the photon as λ , then we can use the relationship between wavelength and frequency where c is the speed of light in a vacuum

$$\lambda = \frac{c}{v}.$$

We combine these two equations to get a relationship between wavelength and energy

$$\lambda = \frac{c}{v} = \frac{hc}{hv} = \frac{hc}{E}. \quad (2.1)$$

Putting in values of $h = 4.135 \times 10^{-15}$ eV-s, and $c = 2.998 \times 10^{10}$ cm/s, we get

$$\lambda = \frac{hc}{E} = \frac{(4.135 \times 10^{-15})(2.998 \times 10^{10})}{E} = \frac{1.24}{E} \mu\text{m}.$$

When a photon comes into contact with a semiconductor, there are many possible interactions. If the photon has enough energy it can elevate an electron from the valence band to the conduction band of the semiconductor and produce an electron-hole pair and thus power or electrical energy. If the photon doesn't have enough energy it can pass through the semiconductor material making the material seem transparent. The photon can also interact with the semiconductor lattice and produce heat. Solar cell technology focuses on the first possibility, the production of electrical energy.

2.1 Function

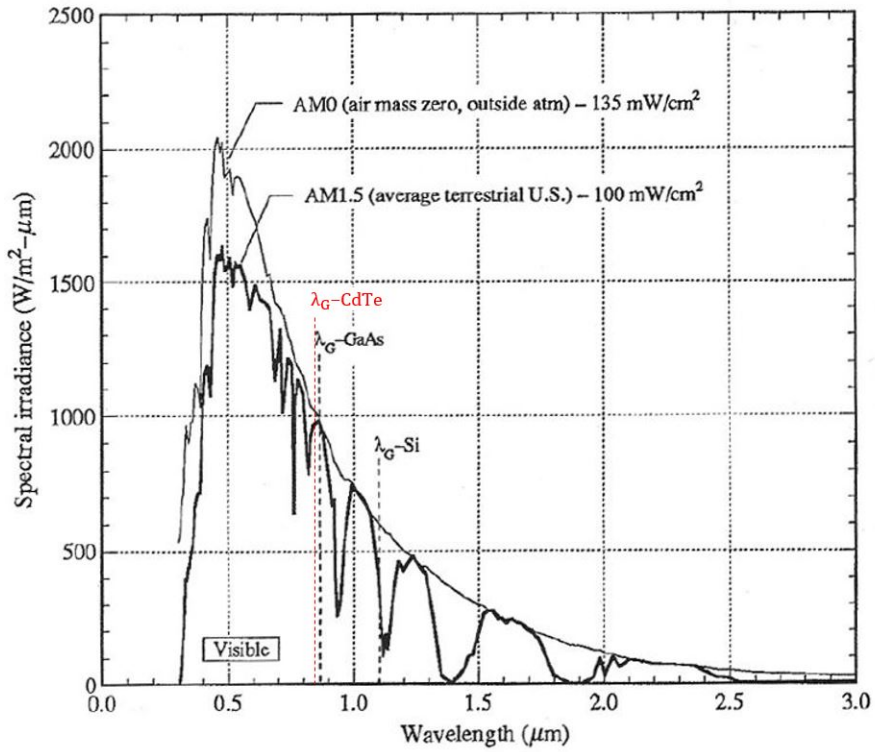


Figure 2.1: Solar Spectral Irradiance (Pierret (1996))

When light hits semiconductor material the photons may be absorbed or propagate through the material. This is determined by the relationship between the energy of the photon and the band-gap energy of the semiconductor material. If the energy of the photon is equal to the band-gap energy of the semiconductor material, then the photon may elevate an electron from the valence band to the conduction band and thus produce an electron-hole pair in the semiconductor material.

Figure 2.1 shows the spectral distribution of the sun's energy that reaches the surface of the earth. The air mass zero (AM0) curve is the measured radiant energy outside of the earth's atmosphere. The AM1.5 curve has been normalized to

give a total spectral power density of 100 mW/cm^2 . It represents the average terrestrial condition in the United States. A small box near the bottom of the graph shows where the visible spectrum of light falls (between 0.4 and $0.7 \mu\text{m}$). Also shown are the band-gap energy levels of three semiconductor materials, cadmium telluride (CdTe), gallium arsenide (GaAs) and silicon (Si) denoted as λ_G . Those energy levels illustrate the relationship between energy and wavelength, specifically, the greater the wavelength, the lower the energy. Note that $\lambda_G\text{-Si}$ is at a greater wavelength than $\lambda_G\text{-GaAs}$ and $\lambda_G\text{-CdTe}$. This reflects the fact that the band-gap energy of Si is lower than the bandgap energies of GaAs and CdTe. Therefore more of the sun's light may be converted to power by Si than by GaAs or CdTe (Pierret (1996)).

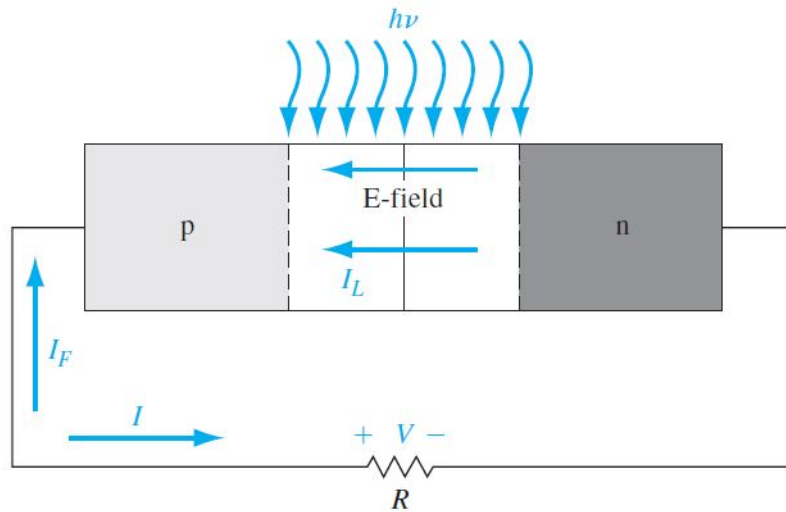


Figure 2.2: A p-n Junction Solar Cell with Resistive Load (Neamen (2012))

Now we look at a simple p-n junction (shown in Figure 2.2). Note that this p-n junction has a resistive load (R) and the bias applied to the junction is zero. Even without an applied bias, there is an electric field (E-field) in the space charge region. Light or photon radiation (shown as $h\nu$) may create electron-hole pairs in the space

charge region that will be swept out. These electron-hole pairs will produce a current (I_L) in the reverse-biased direction called a photocurrent. The photocurrent creates a voltage drop that puts the p-n junction into forward bias which creates a forward bias current. This is shown in Figure 2.2 as I_F (vertical arrow on the left). The net current in the p-n junction is given as $I = I_L - I_F$. Now we introduce the ideal-diode equation (Neamen (2012)) to find an expression for the forward-bias current

$$I_F = I_S \left[\exp \left(\frac{eV_a}{kT} \right) - 1 \right]$$

where I_S is the reverse saturation current, e is the electronic charge (magnitude), V_a is the applied voltage, k is Boltzmann's constant, and T is the temperature in degrees Kelvin. We make a substitution to get

$$I = I_L - I_F = I_L - I_S \left[\exp \left(\frac{eV_a}{kT} \right) - 1 \right]. \quad (2.2)$$

As the diode (p-n junction) becomes forward biased, the electric field in the space charge region, E-field, is decreased. But E-field doesn't go to zero. The photocurrent, I_L , and the net current, I , both stay in the reverse-biased direction. We consider two limiting cases, where the resistance goes to zero and where the resistance goes to infinity. The case where the resistance is equal to zero is known as the short-circuit current (I_{sc}) and we have that $I = I_{sc} = I_L$. The case where the resistance goes to infinity is where the net current is zero and the resulting voltage is known as the open-circuit voltage (V_{oc}). In this case the photocurrent is balanced by the forward-biased junction current which produces

$$I = 0 = I_L - I_S \left[\exp \left(\frac{eV_{oc}}{kT} \right) - 1 \right].$$

When we solve this equation for V_{oc} we obtain

$$V_{oc} = \left(\frac{kT}{e} \right) \ln \left(1 + \frac{I_L}{I_S} \right).$$

Figure 2.3 shows a plot of the current vs. voltage (I - V) from equation (2.2). We have included the short-circuit current (I_{sc}) and the open-circuit voltage (V_{oc}) in the figure. Given that power is equal to current times voltage, we can express the power delivered to the load as

$$P = I \cdot V = I_L \cdot V - I_S \left[\exp \left(\frac{eV}{kT} \right) - 1 \right] \cdot V.$$

In order to maximize the power delivered to the load we take the derivative with respect to voltage and set it equal to zero. This gives us

$$\frac{dP}{dV} = 0 = I_L - I_S \left[\exp \left(\frac{eV_m}{kT} \right) - 1 \right] - I_S V_m \left(\frac{e}{kT} \right) \exp \left(\frac{eV_m}{kT} \right).$$

We use trial and error in order to find the value of V_m that produces the maximum power. When we take I_m equal to the current given the value of V_m we get the maximum power rectangle shown in Figure 2.3.

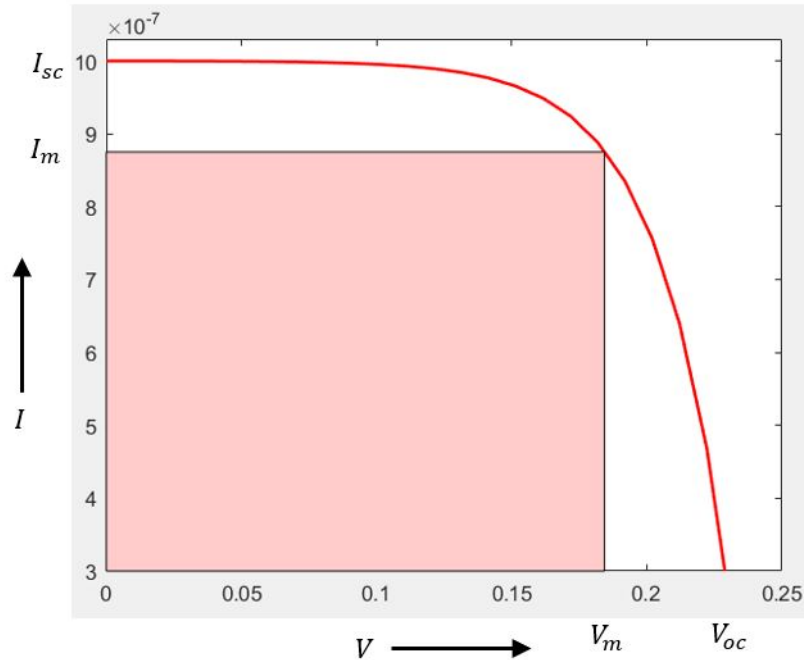


Figure 2.3: Maximum Power Rectangle of the Solar Cell $I - V$ Characteristics.

2.2 Defects

Some of the mechanisms that contribute to solar cell degradation are listed here (Jordan and Kurtz (2012)).

- Encapsulant browning
- Bad solder bonds
- Ethylene Vinyl Acetate (EVA) browning
- Light-induced degradation
- Soiling effects - Dust and dirt covering the solar cell mitigated by regular cleaning.
- Oxygen contamination in the bulk of the Si junction (rapid)
- Ultraviolet exposure (slow) (Osterwald *et al.* (2002))
- Increase in series resistance (Morita *et al.* (2003))
- Corrosion and interconnect breakage
- Electrical component failure
- Thermomechanical fatigue of the interconnects
- Antireflective coating
- Front delamination
- Inherent junction degradation
- Climate conditions

PV education reports that a photovoltaic (PV) module's operating life is largely determined by the stability and resistance to corrosion of the materials from which it is constructed. They report that most of the reasons for failure are related to water ingress or temperature stress. A gradual degradation in module performance can be caused by: 1. Increases in R_s (series resistance) due to decreased adherence of contacts or corrosion (usually caused by water vapor); 2. Decreases in R_{sh} (shunt resistance) due to metal migration through the p-n junction; 3. Antireflection coating deterioration (Honsberg and Bowden (2019))

Pollutants diffuse into the cell, become ionized and ruin (in the long run) the functionality of the cell. Some of these pollutants are positively and negatively charged chlorine, oxygen, sulfur, arsenic (Cl^\pm , O^\pm , S^\pm , As^\pm , ...) (Ringhofer (2018)).

By volume, dry air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.04% carbon dioxide, and small amounts of other gases. The other constituents, which include the inert elements neon, helium, krypton, xenon, as well as hydrogen and some other compounds, such as methane, sulfur dioxide, and various oxides of nitrogen, that come from biological and industrial processes, are present in extremely small fractions, a few parts per million or less (Neiburger *et al.* (1982)).

List of items that degrade cadmium telluride (CdTe) (Ringhofer (2018)):

- Cu_i^+ (copper interstitial)
- Cu_{Cd}^- (copper cadmium)
- Cd_i^{+2} (cadmium interstitial)
- $Cu_i + Cu_{Cd}$ (copper interstitial - copper cadmium)

- Cu_i^0 (copper interstitial)
- Cu_{Cd}^0 (copper cadmium)
- Cl_{Te}^+ (chlorine telluride)
- Cl_i^+ (chlorine interstitial)
- Cl_i^0 (chlorine interstitial)
- Cl_i^- (chlorine interstitial)
- $\text{Cl}_i + \text{Cl}_{Te}^0$ (chlorine interstitial - chlorine telluride)
- $\text{Cl}_i + \text{Cl}_{Te}^{+1}$ (chlorine interstitial - chlorine telluride)
- $\text{Cl}_i + \text{Cl}_{Te}^{+2}$ (chlorine interstitial - chlorine telluride)
- $\text{Cl}_i + \text{Cu}_{Cd}^0$ (chlorine interstitial - copper cadmium)
- $\text{Cl}_i + \text{Cu}_{Cd}^{+1}$ (chlorine interstitial - copper cadmium)
- $\text{Cl}_i + \text{Cu}_{Cd}^{+2}$ (chlorine interstitial - copper cadmium)
- $\text{Cl}_i + \text{Cu}_{Cd}^{+2}(\text{Q2})$ (chlorine interstitial - copper cadmium)

The superscripts denote the ionic charges; $+$ denotes +1 Cation (a positively charged ion), and $-$ denotes -1 Anion (a negatively charged ion).

2.3 Lifetime Tests

Around 1980, the Jet Propulsion Laboratory (JPL) in California conducted a block buy program where they procured PV modules and tested them using various

procedures (Wohlgemuth (1994)). The first step in module testing is outdoor exposure, since this is where the modules have to work. However, outdoor exposure takes too long and varies from location to location. Therefore, standardized accelerated tests were developed. In the first step to designing accelerated environmental tests, extreme care was taken to insure that the test related to both acceleration of the environment that the product was to be exposed to as well as to the mechanisms by which the environmental stress causes failure in the product. Manufacturers use the accelerated tests as quick feedback in the development of more reliable modules. By designing modules to pass the accelerated tests, production modules may no longer exhibit the early field failures caused by the failure mechanisms that the accelerated tests were designed to stress.

The next step is field deployment of modules that successfully pass the accelerated environmental tests. Once again, field failures are likely to occur, but this time the modules will probably work for a much longer time. These new failures have to be analyzed, failure mechanisms identified and new or modified accelerated environmental tests developed.

Assessment of module field failures has always been an important part of PV reliability. This leads to the whole field of Accelerated Lifetime Testing (ALT), where time is artificially accelerated in a laboratory experiment by changing environmental conditions, such as ambient temperature (TamizhMani and Kuitche (2013)). Initial identification of failure modes was a key part of the development of accelerated stress tests and ultimately the module qualification tests (IEC 61215). Because the qualification tests have now been in use for many years, we would expect that some of the identified failure modes would be reduced or eliminated in more modern module

types. On the other hand as new module types are implemented and deployment conditions change, we expect either new failure modes or at least changes in the frequency of the different modes (Wohlgemuth (2018)).

An accelerated lifetime test is described in Albin (Albin (2011)). In order to ascertain the long term reliability of modules based upon cadmium sulfide/cadmium telluride (CdS/CdTe), cells of this basic design were exposed to 1-sun illumination under open-circuit, V_{oc} , bias and acceleration temperatures of 60 - 120 °C for times exceeding 1000 hours. Under field-use conditions, series-connected cells nominally see voltages somewhat less than V_{oc} , thus, open-circuit conditions represent an additional form of acceleration. It is here that computational models of degradation play an important role. ALT testing, as well as computational models, necessarily depend on some simplifying physical assumptions. It is, however, rather easy to "accelerate" time in a computational model by simply using larger time scales.

2.3.1 Pictures

This section shows some examples of PV defects. Also shown are components of solar cell modules where some of the defects can occur. Figure 2.4 shows a solar panel on the ASU Tempe campus near the Hayden Library. Figure 2.5 is a close up of the same solar panel. The solar cell appears to have suffered from front delamination.



Figure 2.4: Defective Solar Panel
Near Hayden Library.



Figure 2.5: Closeup Showing
Front Delamination of Solar
Panel.

Figures 2.6 and 2.7 show some of the components of the solar collection system on the Apache parking structure on the ASU Tempe campus. These pictures show how many electrical and mechanical components are used in order to transport the electricity to the final load. Notice the mechanical hydraulics in figure 2.6 that support the tilting of a series of PV modules in order to receive direct sunlight throughout the day. All of these components are susceptible to failure thus contributing to solar cell degradation.



Figure 2.6: Electrical and Mechanical Components of PV Modules at ASU Apache Parking Structure.



Figure 2.7: Electrical Components of PV Modules at ASU Apache Parking Structure.

2.4 A Simple Model Equation

We will now consider a simple example for the time evolution of degrading defects. We will restrict ourselves for the moment to the zero-dimensional case, ignoring the spatial transport of defects and assuming a spatially homogeneous material. (Spatial transport and diffusion will of course be essential in modeling defects later on.) We consider a simple reaction system modeled by a system of ordinary differential equations. Given five species we consider two reactions of the form:



Here we have two particles (species 1 and species 2) that react to form a particle of species 3. The resulting particle of species 3 can combine with a particle of species 1 again to form two particles of type 4 and 5 (species 4 and species 5). While there is not much physical relevance to this example, it serves as an example of binary reactions where two molecules combine into one and two molecules produce two different molecules. We also consider the corresponding inverse reactions. This

will give us the following five differential equations for the mol densities, u_j , of the species:

$$\begin{aligned}
 \dot{u}_1 &= -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\
 \dot{u}_2 &= -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\
 \dot{u}_3 &= \alpha_1^f u_1 u_2 - \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\
 \dot{u}_4 &= \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \\
 \dot{u}_5 &= \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5
 \end{aligned} \tag{2.3}$$

Where α is the coefficient of the reaction. The subscript of α indicates the reaction number and the superscript indicates whether the reaction is forward or backward. For example α_1^f denotes the coefficient of the first reaction going forward. A key tool to encode the structure of a given set of reactions (i.e. which species react with other species) is the stoichiometry matrix (see Section 3.1). A row of this matrix corresponds to a single reaction and, within each row, an entry of negative one corresponds to a particle lost and an entry of one corresponds to a particle gained in the reaction. Using this example, the stoichiometry matrix will be as follows:

$$S = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 \end{pmatrix}$$

Notice that the first row describes the first reaction where species one and two lose one element and species three gains one element. The second row corresponds to the second reaction. The columns correspond to the species participation in the reaction. In general, given N species and K reactions, the stoichiometry matrix will be a $K \times N$ matrix.

We consider the results of a MATLAB program which models binary reactions while ensuring that correct quantities are conserved. We wrote the program for a variable number of species and a variable number of reactions.

The input to the program is:

S = the stoichiometry matrix describing the different reactions,
 α_β^f = the coefficients ($\beta = 1 : K$) for the forward reactions,
 α_β^b = the coefficients ($\beta = 1 : K$) for the backward reactions.

Since we will consider binary reactions only, the resulting ODE system will exhibit a quadratic and vector-valued right hand side. Each differential equation is then of the form

$$\dot{u}_n = \vec{u}^T A_n \vec{u} + b_n^T \vec{u}.$$

where for the first species the matrix A and the vector b are of the form

$$A_1 = \begin{pmatrix} 0 & -\alpha_1^f & -\alpha_2^f & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha_2^b \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{and } b_1^T = (0 \ 0 \ \alpha_1^b \ 0 \ 0)$$

We start by computing the solution using the Euler method with equations (2.3). Then we used the stoichiometry matrix and computed the matrices A and b . Then we computed the solution using the matrices A and b and compared the solutions and the CPU time for each computation. We used some "vectorized" commands in MATLAB from Higham (Higham (2001)).

The solutions were identical up to machine precision. The time was vastly different. Using the Euler method the time was 4.737902 seconds. Using the matrices the

time was 0.460772 seconds. This comparison was completed using only five species and two reactions. Figures 2.8 and 2.9 show the two output figures using a surface plot. Figure 2.10 shows the solution in two dimensions.

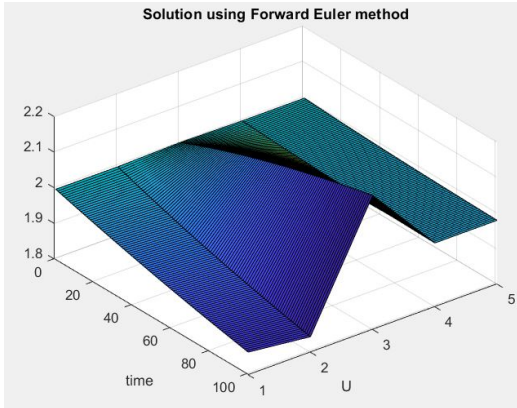


Figure 2.8: Solution Using the Forward Euler Method

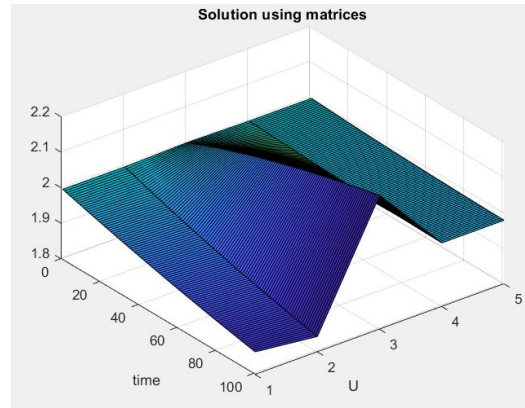


Figure 2.9: Solution Using Matrices

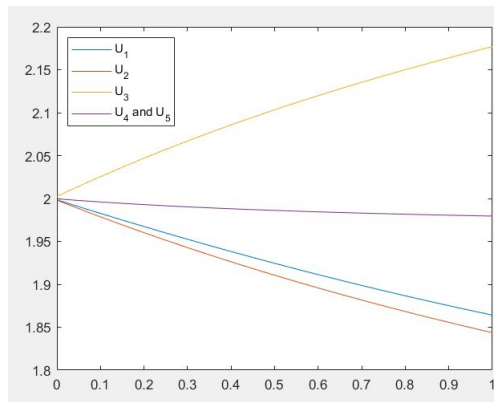


Figure 2.10: Forward Euler Solution in 2-D

Chapter 3

STOICHIOMETRY THEORY

In this section we formulate systems of reaction equations based on binary reactions which describe chemical reactions of defects and ionization processes (i.e. the reaction of ions with free electrons). Since the number of molecules in these reactions is not conserved, the resulting equations constitute a non-conservative system. To develop physically relevant models, it is important to identify which components of the mathematical solution of the resulting differential equations are actually conserved. The key to this is basic stoichiometry theory. We first give a definition and overview of stoichiometry theory and derive a general principle to determine which components of the solution of the model equations are conserved for a system consisting of an arbitrary number of species and an arbitrary number of reactions.

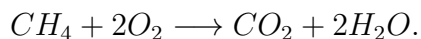
3.1 Stoichiometry Theory

Stoichiometry is the area of study that examines the quantities of substances consumed and produced in chemical reactions (Brown (2008)). This section describes how stoichiometry theory is used to symbolize chemical reactions. Reaction stoichiometry describes how to determine quantity relationships between reactants (Flowers *et al.* (2018)).

3.1.1 Writing Chemical Equations

We write chemical equations to describe the process of an atom gaining or losing an electron, or combining with another atom or atoms to form molecules. The symbols of the atoms are changed or combined with the symbols of other atoms. In this

way we create a chemical equation or formula that represents the species involved in the reaction. We are careful to include not only the types of species involved in the reaction but the quantities of each specie involved. We also wish to balance the chemical equation in order to be in compliance with the law of conservation. We will consider an example reaction where the species are one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) combine to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). We can represent this reaction with the following chemical equation



Here we can name some fundamentals for chemical equations:

1. Species being reacted upon are reactants and they are represented by their formulas on the left side of the arrow.
2. Species that are the result of the reaction are called products and they are represented by their formulas on the right side of the arrow.
3. We use a plus sign (+) to separate each specie on either side of the equation.
4. We use an arrow (\longrightarrow) to separate the reactants and products (the left and right) sides of the equation.
5. Coefficients are used to represent the numbers of each individual reactant and product species.

3.1.2 *Balancing Equations*

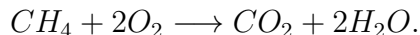
In the example above we have a balanced chemical equation. We may note that the number of atoms of each specie is the same on the ractant side and the product

side of the equation. Balancing chemical equations is required by conservation of matter. We can confirm that a chemical equation is balanced by summing the number of atoms on both sides of the equation. If they are equal, then the equation is balanced. In order to correctly count the number of atoms for each specie we multiply the coefficient by the subscript of the specie. We look at another example.

Again, we look at the reaction between methane and oxygen that produces carbon dioxide and water. We see that both CO_2 and H_2O contain the species oxygen. We follow the formula and multiply the coefficient by the subscript as follows:

$$\left(1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}}\right) + \left(2 \text{ H}_2\text{O molecules} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}}\right) \\ = 4 \text{ O atoms.}$$

We see that this equation is balanced, as shown here:



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$, yes
H	$1 \times 4 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$, yes

We consider a system of general binary reactions of the form



Two molecules or atoms, one each of species 1 and 2, react and form either two molecules, one each of species 3 and 4, or a single molecule of species 3. The reaction is, in general, reversible and time scales are given by reaction rates. Considering a

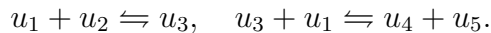
system of N species the evolution of the mol numbers $u_n(t)$ of species n are given by the ODE system

$$\frac{d}{dt}\vec{u}(t) = \vec{r}(\vec{u}), \quad \vec{u} = (u_1, \dots, u_N), \quad \vec{r} = (r_1, \dots, r_N),$$

where the vector function \vec{r} is quadratic. In general, \vec{r} will be of the form

$$r_n = \vec{u}^T A_n \vec{u} + \vec{b}_n^T \vec{u}, \quad n = 1 : N.$$

We again consider the example of Section 2.4. A reaction system with five species and two reactions of the form



The resulting ODE system is of the form

$$\begin{aligned} \dot{u}_1 = r_1 &= -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_2 = r_2 &= -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\ \dot{u}_3 = r_3 &= \alpha_1^f u_1 u_2 - \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_4 = r_4 &= \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \\ \dot{u}_5 = r_5 &= \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \end{aligned} \tag{3.1}$$

with the α_k^f and α_k^b , $k = 1, 2$ the reaction rates for the forward and backward reactions.

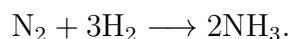
To illustrate the structure, we give a simple example in section 3.2.

3.1.3 Reaction Stoichiometry

Chemical equations give us information regarding the species that are reactants and species that emerge from the reaction as products. Each coefficient tells us the relative amounts of each of the species involved in the reaction. This allows us to perform a quantitative assessment of the amounts of species consumed and produced by each reaction. This is known as the reaction's stoichiometry. Stoichiometry is

a term that was derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure") (Flowers *et al.* (2018)).

We can use a balanced chemical equation to find out how much of one specie is required to combine with a given amount of another specie on the reactant side and give a certain amount of product specie. We use the coefficients in the balanced equation to produce the stoichiometric factors that allow us to compute the desired quantity. We illustrate this with an example. Consider the reaction of nitrogen and hydrogen to produce ammonia:



This shows that for every two ammonia molecules we need three hydrogen molecules. This gives us a 2:3 ratio. The stoichiometric factors are independent of the units involved as long as the units used to measure the ammonia molecules are the same as the units used to measure the hydrogen molecules:

$$\frac{2 \text{ NH}_3 \text{ molecules}}{3 \text{ H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}.$$

The stoichiometric factors allow us to compute the number of ammonia molecules produced from a given number of hydrogen molecules. Or, we can compute the number of hydrogen molecules required to produce a given number of ammonia molecules. This can be extended to any pair of species in any chemical equation.

3.1.4 Percent Yield

The theoretical yield of any reaction is the amount of species produced by a reaction as calculated by the stoichiometry of the balanced chemical equation that governs that reaction. Often, the theoretical yield of a chemical reaction is more

than the actual yield. This is due to several reasons. Some reactions are inherently inefficient because we have simplified the actual reaction by not taking into account side reactions that generate other products. Other reactions are incomplete because of various physical considerations. Some products are hard to measure without some loss. Percent yield is the extent that the theoretical yield of a reaction is achieved:

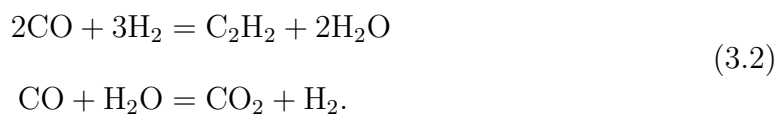
$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%.$$

Actual and theoretical yields may be expressed in any unit, such as mass or molar amounts. We must use the same units in both the actual yield and the theoretical yield in order to get an accurate percent yield.

3.2 Conservation Properties

To derive physically relevant simulation tools it is essential to numerically conserve physically conserved quantities. In addition, the understanding of which quantities are conserved by the model equations will be necessary for the formulation and development of asymptotically preserving schemes in Chapter 8. This raises the question of how to find all possible conserved quantities in a complex reaction system given a set of model equations of the form (3.1). The key to this venue is the use of the stoichiometry matrix outlined below.

We will begin by looking at a complex chemical reaction equation and talk about the conservation properties preserved through stoichiometry theory. Then we will look at a simple model of a generic reaction. First we will consider the chemical reaction equation (Erdi and Toth (1989)).



The three atoms involved in this reaction are hydrogen (H), oxygen (O), and carbon (C). The five chemical compounds in this reaction are carbon monoxide (CO), dihydrogen (H₂), acetylene (C₂H₂), water (H₂O), and carbon dioxide (CO₂).

We now use the atomic matrix to describe the atomic structure of the components of this reaction

$$Z \equiv \begin{array}{c} \text{CO} \quad \text{H}_2 \quad \text{C}_2\text{H}_2 \quad \text{H}_2\text{O} \quad \text{CO}_2 \\ \text{H} \\ \text{O} \\ \text{C} \end{array} \begin{pmatrix} 0 & 2 & 2 & 2 & 0 \\ 1 & 0 & 0 & 1 & 2 \\ 1 & 0 & 2 & 0 & 1 \end{pmatrix}$$

Notice that the first row shows how many hydrogen atoms are in each of the five chemical compounds. The second row shows how many oxygen atoms and the third row is for the carbon atoms. The columns show how many of each atom are in each compound.

We can describe the structure of the reactions with a matrix made up of reaction vectors called the stoichiometric matrix

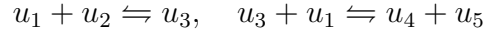
$$\gamma = \begin{array}{c} \text{CO} \\ \text{H}_2 \\ \text{C}_2\text{H}_2 \\ \text{H}_2\text{O} \\ \text{CO}_2 \end{array} \begin{array}{cc} R1 & R2 \\ \begin{pmatrix} -2 & -1 \\ -3 & 1 \\ 1 & 0 \\ 2 & -1 \\ 0 & 1 \end{pmatrix} \end{array} .$$

Notice that the *R1* vector describes the first reaction as two of the CO molecules and three of the H₂ molecules are put into the reaction (negative values) to produce one C₂H₂ molecule and two H₂O molecules (positive values). The *R2* vector describes

the second reaction as one CO molecule and one H₂O molecule are put into the reaction (negative) to produce one H₂ molecule and one CO₂ molecule (positive). The conservation law of atomic balance says that the number of atoms should be the same on both sides of each of the reactions. We can ensure that this conservation law is satisfied by multiplying Z and γ using normal matrix multiplication and see that the product is zero:

$$Z\gamma = \begin{bmatrix} 0 & 2 & 2 & 2 & 0 \\ 1 & 0 & 0 & 1 & 2 \\ 1 & 0 & 2 & 0 & 1 \end{bmatrix} \begin{bmatrix} -2 & -1 \\ -3 & 1 \\ 1 & 0 \\ 2 & -1 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}$$

We recall our example from Section 3.1.2. Given five species and two reactions as follows:



We have the following five differential equations:

$$\begin{aligned} \dot{u}_1 &= r_1 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_2 &= r_2 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\ \dot{u}_3 &= r_3 = \alpha_1^f u_1 u_2 - \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_4 &= r_4 = \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \\ \dot{u}_5 &= r_5 = \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \end{aligned} \tag{3.3}$$

The stoichiometry matrix (see Section 3.1) will be as follows:

$$\mathbf{S} = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 \end{pmatrix}$$

Given N species and K reactions, the stoichiometry matrix will be a $K \times N$ matrix. The first row corresponds to the first reaction and the second row corresponds

to the second reaction. The columns correspond to the species participation in the reaction. Notice that the first row describes the first reaction where species one and two lose one element and species three gains one element.

For the development of an asymptotic theory in the following sections and for the purpose of numerical accuracy it is important to identify the conserved quantities of the system, i.e. we are looking for vectors \vec{c} such that

$$\vec{c}^T \frac{d}{dt} \vec{u} = \vec{c}^T \vec{r}(\vec{u}) = 0$$

holds for all solutions \vec{u} . Fortunately the conservation vectors \vec{c} are a property of the reaction structure and independent of the state \vec{u} . They can be determined via the use of the stoichiometry matrix. For a system of K reactions and N species the stoichiometry matrix S is a $K \times N$ matrix, and is constructed as follows:

For each lost molecule in the forward reaction number k the k^{th} row of S contains an entry of negative one and for each gained molecule an entry of one. So, for the example above, S is a 2×5 matrix of the form

$$S = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 \end{pmatrix} .$$

The basic idea of determining the conservation vectors is to consider a system for mass densities instead of molecule numbers. If each molecule of species n has a mass w_n the total mass of the system has to be conserved. Setting the mass density vector to \vec{y} we have $\dot{y}_n = w_n r_n(\vec{u})$, $n = 1 : N$, and we have conservation of the total mass, expressed by

$$\frac{d}{dt} \sum_{n=1}^N y_n = \sum_{n=1}^N w_n r_n = 0 .$$

To actually use the equivalent system for the masses y_n is not practical because of the large difference in the masses of the individual reactants. If the reaction is of the form that an uncharged atom and an electron create a negative ion the mass ratio between the atom and the electron is of the order of 10^{20} . *However, we do not need to use the actual physical masses of the involved atoms, but can use any set of virtual masses (or weights) w_n , as long as they are consistent with the reaction system.* This consistency condition is obtained from the stoichiometry matrix S . If the reaction is of the form $s_1 + s_2 \rightleftharpoons s_3$, then $w_1 + w_2 = w_3$ has to hold to conserve mass in the reaction. In the example above this would give the two consistency conditions $w_1 + w_2 = w_3$ and $w_1 + w_3 = w_4 + w_5$ for the two reactions. So the consistency conditions for the weights w_n , considering all reactions, are given by the equation $S\vec{w} = 0$. This gives

$$\vec{w}^T \vec{r} = 0 \quad \forall \vec{w} : S\vec{w} = 0 .$$

So all conserved quantities can be computed by finding a basis of the nullspace $\mathcal{N}(S)$, yielding in general J linearly independent vectors $\vec{c}_1, \dots, \vec{c}_J$ (J being the dimension of $\mathcal{N}(S)$) with

$$\frac{d}{dt}(\vec{c}_j^T \vec{u}) = \vec{c}_j^T \vec{r}(\vec{u}) = 0, \quad j = 1 : J, \quad \forall \vec{u} .$$

For the example above the stoichiometry matrix S is 2×5 and we obtain a basis for the nullspace of S as

$$c_1 = \begin{pmatrix} -1 \\ 2 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad c_2 = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad c_3 = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 1 \end{pmatrix},$$

which implies the three conservation relations

$$\frac{d}{dt}(-u_1 + 2u_2 + u_3) = 0, \quad \frac{d}{dt}(u_1 - u_2 + u_4) = 0, \quad \frac{d}{dt}(u_1 - u_2 + u_5) = 0,$$

which can be easily verified from the original equations (3.3).

Of course, any linear combination of the basis vectors \vec{c}_j will yield another element of $\mathcal{N}(S)$, and we obtain an infinite number of conserved quantities, which are all linear combinations of the J linearly independent basis vectors.

The importance of this approach is that all conserved quantities can be computed from the stoichiometry matrix S , which is a function of the structure of the reaction system only. So, the subspace of conserved quantities can be computed a priori, independent of the current state of the solution \vec{u} .

DEFECT TRANSPORT MODELS

To simulate the degradation of solar cells it is essential to consider the migration of defects in addition to the reaction processes. In this work we restrict ourselves to diffusion-convection models for the transport picture. Given the density, $u_n(x, t)$, for species number n (which now depends also on the spatial variable, x) the resulting model equations (van Roosbroeck (1950)) are of the form

$$\partial_t u_n(x, t) = T_n u_n + \left(\frac{1}{\epsilon}\right) r_n(u_n), \quad n = 1 : N, \quad (4.1)$$

with the diffusion operator T_n given by

$$T_n \vec{u} = \nabla_x \cdot [D_n \nabla_x u_n + z_n \mu_n \nabla_x V u_n], \quad n = 1 : N, \quad (4.2)$$

and the quadratic reactions term defined as in Section 2.4

$$\dot{u}_n = r_n = \vec{u}^T A_n \vec{u} + b_n^T \vec{u}.$$

D_n and μ_n in the definition (4.2) of the transport operator denote the diffusion coefficient and the mobility of a molecule of species n . The motion of the particle is in addition driven by a convection term, due to the possible electrical charge of the molecule. z_n denotes the charge of a particle/molecule of species n . The term $\nabla_x V(x, t)$ in (4.2) denotes the electric field (the gradient of the electrodynamic potential), which is given in terms of the charges produced by the defects via the Poisson equation

$$-\nabla_x \cdot (\kappa \nabla_x V(x, t)) = \sum_{n=1}^N z_n u_n + D(x). \quad (4.3)$$

Here κ denotes the usual dielectricity constant and the time independent function $D(x)$ denotes some background concentration of immobile carriers (determining whether we are in a p-type or n-type region). We note that coupling the diffusion reaction system (4.1) to the Poisson equation (4.3) via the electric field results in the transport problem becoming nonlinear, i.e. $V = V(\vec{u})$ holds.

Finally, the dimensionless parameter ϵ in (4.1) denotes the separation of the transport and the reaction time scales. In a lifetime stress test, defects will diffuse on a time scale of months or years whereas reactions will happen on a scale of minutes or hours. Therefore $\epsilon \ll 1$ will hold.

Chapter 5

ASYMPTOTICS

In this chapter we consider the analysis of the stiff (in time) reaction diffusion system presented in Chapter 4. The stiffness arises from the fact that reactions occur on a much faster time scale than the spatial transport. The goal is to derive the asymptotic behavior of the solution on the slow (diffusion) time scale by looking at the reduced equation ($\epsilon = 0$). The relevance of the analysis in this chapter is twofold. On one hand the results of this chapter will give guidance for the development of an efficient numerical solution of the model equations. A straightforward numerical approach to the equations turns out to be prohibitive due to the vastly different time scales. On the other hand, the resulting reduced problem gives insight into which mechanisms are really responsible for the large time degradation of the solar cell. We note that the analysis below is not restricted to diffusion transport models of the form (4.2). In many simulations more detailed transport models based on particle models and kinetic equations are used on short time scales (Dimarco and Pareschi (2011), Ascher *et al.* (1997), Caffisch *et al.* (1997)). In this section we only use the conservation properties and certain coercive properties of the transport operator. The analysis translates therefore immediately to these more detailed models. In Section 5.1 we outline the basic idea of the asymptotic analysis. The reactions preserve a set of quantities, given by stoichiometry theory, discussed in Chapter 3. To compute the correct steady states for $t \rightarrow \infty$ it is imperative that these quantities are also preserved by the reduced system. In Appendix A we illustrate the results of Section 5.1 with a simple example. In Section 5.4 we present a proposition showing subspace conservation and a proposition showing that the reduced equation conserves the cor-

rect quantities (given by stoichiometry theory). In Section 5.5 we discuss an approach to the numerical solution of the reduced problem and show that the numerical scheme is order 1 consistent. Although we will restrict ourselves to very small "toy" problems for the computational examples in this and the next chapter, it should be pointed out the following analysis and approach is scalable, i.e. leading to a numerical method which can solve rather large reaction transport systems in multiple spatial dimensions at a reasonable computational cost.

5.1 Basic Approach

There exists a basic methodology to derive asymptotic large time models for dynamical systems of the form (4.1). This methodology is originally due to Maxwell and Chapman and Enskog (Maxwell (1878), Rosenbourn (1941), Enskog (1911b)), and was originally developed to derive macroscopic models in gas dynamics such as the compressible Euler equations and the Navier-Stokes equations from the underlying Boltzmann equation. This basic methodology is of the following form:

Given a dynamical system of the form

$$\partial_t u = Tu + \left(\frac{1}{\epsilon}\right) r(u) \tag{5.1}$$

1. Find the conserved quantities, i.e. find a matrix C such that $C^T r(u) = 0$ holds for all u . The slow evolution is then given by the equation

$$\partial_t(C^T u) = C^T T u . \tag{5.2}$$

2. Consider in zero-th order the equation on the fast $O(\frac{t}{\epsilon})$ time scale

$$\partial_t u = \frac{1}{\epsilon} r(u), \quad \partial_\tau u = r(u) + O(\epsilon), \quad \tau = \frac{t}{\epsilon} .$$

The large time solution is given by the steady state, given by the equation $r(u) = 0$.

3. Parameterize this solution by a parameter p , i.e. $r(u) = 0 \iff u = u_{eq}(p)$.
4. Close equation (5.2) by using this parameterization, giving

$$\partial_t(C^T u_{eq}(p)) = C^T T u_{eq}(p) \quad (5.3)$$

Equation (5.3) is a closed equation on the large $O(t)$ time scale for the parameter p , as long as the number of columns in the matrix C equals the dimension of the parameter vector p . (For infinite dimensional problems this must be verified by proving the existence of a Fredholm alternative.)

We have basically taken care of step 1 in the above algorithm (the computation of the conserved quantities and the matrix C) in Section 3.2 via the stoichiometry matrix. The basic problem with this methodology in the context of solar cells and general reaction-transport systems lies in step 3 of the above algorithm. In the case of classical gas dynamics, the null manifold of $r(u) = 0$ is given by Boltzmann's H-theorem, and given by Maxwellians, parameterized by density, velocity and temperature. In the case of general reaction-transport systems, the parameterization of this manifold would involve the computation of the general solution of a system of N quadratic equations in the case of N species. While this might be possible for small N using computer algebra tools, it is certainly prohibitive for a realistic number of defect species.

The basic idea of the asymptotic solutions developed here, separating the time scales, is to introduce an additional variable, namely the product of the reactions v . While the separation of the time scales for the evolution of concentrations u is inherently a nonlinear problem, depending on the a priori unknown concentrations, the evolution of the reaction product v becomes linear, given the slow scale evolution

of the concentrations u . This problem can be solved using standard linear projection techniques.

This approach has been followed in the context of fluid and rarified gas dynamics by Boltzmann, Maxwell, Chapman and Enskog (Boltzmann (1995) Maxwell (1878) Rosenbourn (1941) Enskog (1911b) Enskog (1911a) Brush (1972)) for the connection between the Boltzmann equation and the compressible Euler equations of gas dynamics. Higher order expansions, leading to the connections between the Boltzmann equation for particles and the Navier-Stokes equations have been derived in the corresponding literature.

We take a second order formulation and make the substitution: $v = (1/\epsilon)r$. This and equation (5.1) gives us the following with the use of the chain rule:

$$\partial_t v = \frac{1}{\epsilon} R(u) \partial_t u = \frac{1}{\epsilon} R(u) (v + Tu)$$

with $R = \frac{\partial r}{\partial u}$ = the Jacobian matrix of $r(u)$. Equation (5.1) becomes

$$\begin{aligned} \partial_t u &= v + Tu, & u(0) &= u^I \\ \partial_t v &= \frac{1}{\epsilon} R(u)(v + Tu), & v(0) &= v^I = \frac{1}{\epsilon} r(u^I). \end{aligned} \tag{5.4}$$

The quasi-steady-state approximation is a standard procedure in the study of chemical reaction kinetics in situations where certain species have a very short time of existence with respect to other species (Bisi *et al.* (2007)). Accordingly, we assume quasi steady state and so $r(u^I) \approx \epsilon \implies v^I = O(1)$.

5.2 The Fundamental Theorem of Linear Algebra

We will use Strang (Strang (1993)) in the following. Consider a system of the form

$$Rx = y, \quad \text{with } R : N \times M$$

The fundamental theorem of linear algebra gives us the following

$$\mathbb{R}^M = \mathcal{N}(R) \oplus \mathcal{R}(R^T),$$

$$\mathbb{R}^N = \mathcal{N}(R^T) \oplus \mathcal{R}(R),$$

where \mathcal{N} denotes the nullspace, \mathcal{R} denotes the range, and \oplus denotes the orthogonal direct sum. This means that $\mathcal{R}(R) = \mathcal{N}(R^T)^\perp$ and also for the transpose, $\mathcal{R}(R^T) = \mathcal{N}(R)^\perp$. This means that any $y \in \mathbb{R}^N$ can be decomposed uniquely into

$$y = y_1 + y_2, \quad y_1 \in \mathcal{N}(R^T), \quad y_2 \in \mathcal{R}(R), \quad y_1^T y_2 = 0.$$

We also have that any $y \in \mathbb{R}^M$ can be decomposed uniquely into

$$y = y_1 + y_2, \quad y_1 \in \mathcal{N}(R), \quad y_2 \in \mathcal{R}(R^T), \quad y_1^T y_2 = 0.$$

We will assume a square matrix R with $N = M$. Then we can define the left and right nullspaces of R as follows. The left nullspace

$$C = \mathcal{N}(R^T) \implies C^T R = 0.$$

The right nullspace

$$G = \mathcal{N}(R) \implies RG = 0.$$

We can also define the $N \times N$ projection matrix $P = G(C^T G)^{-1} C^T$. Using the projection P we have

$$\mathcal{N}(R^T) = \mathcal{R}(R)^\perp = \{z : C^T z = 0\} = \{z : Pz = 0\}$$

$$\mathcal{N}(R) = \mathcal{R}(R^T)^\perp = \{z : Rz = 0\} = \{z : z = Gq\} = \{z : Pz = z\}$$

We can draw the following conclusions:

1. $Rx = y$ only has a solution if

$$\begin{aligned} y \in \mathcal{R}(R) = \mathcal{N}(R^T)^\perp &\iff z^T y = 0 \quad \forall z \in \mathcal{N}(R^T) \\ &\iff C^T y = 0 \iff Py = 0. \end{aligned}$$

Thus, for general y , we solve $Rx = y_1 = (I - P)y \implies Py_1 = 0$.

2. The solution of $Rx = y_1$ is given by

$$x = x_0 + Gq$$

where x_0 is a particular solution of $Rx = y_1$ and Gq is the general solution of $Rx = 0$.

3. If $\text{rank}(R) = \text{rank}(R^T) = K < N$ then $\dim(\mathcal{N}(R)) = \dim(\mathcal{N}(R^T)) = N - K$.

Therefore G and C are $N \times (N - K)$ full rank matrices. We fix the solution of $Rx = y_1$ by requiring

$$C^T x = 0 \iff Px = 0.$$

5.3 Solving the Fast Equations

We split v into the part that is in the nullspace of R and the part that is in the orthogonal complement of the nullspace of R with $v = \tilde{v} + \hat{v}$ with $\tilde{v} = P(u)v$ and $\hat{v} = (I - P(u))v$. We also define $\dot{P} = \frac{d}{dt}P(u(t))$.

We use this and the product rule with equation (5.4) to get

$$\partial_t \tilde{v} = \partial_t (P(u)v) = P(u)\partial_t v + \dot{P}v = P(u)\frac{1}{\epsilon}R(u)(v + Tu) + \dot{P}v$$

$$\begin{aligned}
&= \frac{1}{\epsilon} P(u)R(u)(v + Tu) + \dot{P}v = \dot{P}v \\
\partial_t \hat{v} &= \partial_t((I - P(u))v) = (I - P(u))\partial_t v - \dot{P}v = (I - P(u))\frac{1}{\epsilon}R(u)(v + Tu) - \dot{P}v \\
&= \frac{1}{\epsilon}(I - P(u))R(u)(v + Tu) - \dot{P}v = \frac{1}{\epsilon}R(u)(v + Tu) - \dot{P}v
\end{aligned}$$

By the definition of P and \tilde{v} we have $R(u)\tilde{v} = R(u)P(u)v = 0$. And from equation (5.4) it follows that

$$\partial_t u = \tilde{v} + \hat{v} + Tu, \quad u(0) = u^I, \quad (5.5)$$

$$\partial_t \tilde{v} = \dot{P}(\tilde{v} + \hat{v}), \quad \tilde{v}(0) = v^I \quad (5.6)$$

$$\partial_t \hat{v} = \frac{1}{\epsilon}R(u)(\hat{v} + Tu) - \dot{P}(\tilde{v} + \hat{v}), \quad \hat{v}(0) = v^I. \quad (5.7)$$

Remark: In local equilibrium $r(u^I) = 0$ which implies that $v^I = 0$ which implies that $\tilde{v}(0) = 0$ and $\hat{v}(0) = 0$.

Now we look for the asymptotic solution to this system of differential equations (Holmes (2013)). We multiply equation (5.7) by ϵ to get

$$\epsilon \partial_t \hat{v} = R(u)(\hat{v} + Tu) - \epsilon \dot{P}(\tilde{v} + \hat{v}).$$

We now let $\epsilon \rightarrow 0$ in order to find the reduced, or order 1, equation. This gives us the leading order equation for \hat{v} of

$$R(u)(\hat{v} + Tu) = 0. \quad (5.8)$$

We now use the projections to investigate the dynamical system

$$\epsilon \partial_t v = R(Tu + v), \quad R : N \times N.$$

With C the basis of the left nullspace of R (i.e. $C^T R = 0$) and G the basis of the right nullspace of R (i.e. $RG = 0$). Both C and G are $N \times N - K$ matrices for

a rank K matrix R . The projection P is given by $P = G(C^T G)^{-1} C^T$. According to the fundamental theorem of linear algebra we have

$$\mathcal{N}(R) = \{z : Rz = 0\} = \{z : z = Gq, \forall q \in \mathbb{R}^{N-K}\} = \{z : Pz = z\},$$

$$\mathcal{R}(R) = \mathcal{N}(R^T)^\perp = \{z : y^T z = 0, \forall y \in \mathcal{N}(R^T)\} = \{z : C^T z = 0\} = \{z : Pz = 0\}.$$

We can re-write equation 5.8 as

$$R\hat{v} = -RTu. \quad (5.9)$$

- This has a solution since the right hand side satisfies $PRTu = 0$.
- According to the fundamental theorem of linear algebra, the general solution is given by $\hat{v} = x_0 + Gq$ with q an arbitrary $N - K$ vector. Adding the condition $\hat{v} \in \mathcal{R}(R) \iff P\hat{v} = 0$ gives $Px_0 + Gq = 0 \iff G(C^T G)^{-1} C^T x_0 + Gq = 0$ and therefore $q = -(C^T G)^{-1} C^T x_0$. This uniquely determines q and therefore \hat{v} .
- On the other hand, we can find the unique solution of (5.9) directly by setting $\hat{v} = (P - I)Tu$, giving

$$R\hat{v} = R(P - I)Tu = -RTu, \quad P\hat{v} = P(P - I)Tu = 0,$$

$$P\tilde{v} = \tilde{v}, \quad (I - P)\tilde{v} = 0, \quad P\hat{v} = 0, \quad (I - P)\hat{v} = \hat{v}.$$

Therefore, the unique solution of $R(Tu + \hat{v}) = 0, P\hat{v} = 0$ is given by $\hat{v} = (P - I)Tu$.

Now equations (5.5) and (5.6) become

$$\begin{aligned} \partial_t u &= \tilde{v} + (P - I)Tu + Tu, \\ \partial_t \tilde{v} &= \dot{P}(\tilde{v} + (P - I)Tu) \end{aligned} \quad (5.10)$$

or

$$\begin{aligned}\partial_t u &= \tilde{v} + PTu, & u(0) &= u^I, \\ \partial_t \tilde{v} &= \dot{P}(\tilde{v} - (I - P)Tu), & \tilde{v}(0) &= v^I\end{aligned}\tag{5.11}$$

with

$$P = G(C^T G)^{-1} C^T, \quad C^T R = 0, \quad RG = 0, \quad \forall u.$$

We provide a simple example at Appendix A.

5.4 Conservation

We split spaces by letting $\mathbb{R}^n = \tilde{S} = \hat{S}$. So we have

$$\tilde{S}(t) = \{v : (I - P(t))v = 0\} = \text{span}(G(t)),$$

$$\hat{S}(t) = \{v : P(t)v = 0\} = \{v : C^T v = 0\}.$$

With the following proposition, we show that the subspace \tilde{S} is conserved.

Proposition (Subspace conservation): Consider the system

$$\partial_t v = \dot{P}(t)v + P(t)f\tag{5.12}$$

then $v(t) \in \tilde{S}$ for all t as long as $v(0) \in \tilde{S}$, and $(I - P(0))v(0) = 0$ holds.

Proof. We start with $\partial_t((I - P)v)$ and use the chain rule.

$$\partial_t((I - P)v) = (I - P)\partial_t v - \dot{P}v$$

now we use equation (5.12) to get

$$= (I - P)(\dot{P}v + Pf) - \dot{P}v = (I - P)\dot{P}v + (I - P)Pf - \dot{P}v = (I - P)\dot{P}v + (P - P^2)f - \dot{P}v$$

Recall that $P^2 = P$ by construction and so we have that

$$\partial_t((I - P)v) = (I - P)\dot{P}v - \dot{P}v. \quad (5.13)$$

We just showed that $(I - P)P = 0$. We differentiate with respect to t and use the chain rule to get

$$0 = \partial_t((I - P)P) = (I - P)\dot{P} - \dot{P}P \implies (I - P)\dot{P} = \dot{P}P.$$

We substitute this result into (5.13) and so $\partial_t((I - P)v) = \dot{P}Pv - \dot{P}v = \dot{P}(P - I)v$.

Now we let $w = (P - I)v$ so we have

$$\partial_t w = \dot{P}w.$$

We note that this is a homogeneous equation in the variable w . So, if $v(0) \in \tilde{S}(0)$ then $(I - P(0))v(0) = 0$, and $(I - P(t))v(t) = 0 \implies v(t) \in \tilde{S}(t)$ holds for all time. \square

We use the identity $P(P - I) = 0 \implies \dot{P}(P - I) = P\dot{P}$ combined with the reduced equations (5.11) which gives us

$$\partial_t \tilde{v} = \dot{P}(\tilde{v} + (P - I)Tu) = \dot{P}\tilde{v} + \dot{P}(P - I)Tu = \dot{P}\tilde{v} + P\dot{P}Tu.$$

And so we have

$$\begin{aligned} \partial_t u &= \tilde{v} + PTu, & u(0) &= u^I, \\ \partial_t \tilde{v} &= \dot{P}\tilde{v} - P\dot{P}Tu, & \tilde{v}(0) &= P(u^I)v^I. \end{aligned} \quad (5.14)$$

The equation for \tilde{v} , equation (5.14), is of the form of equation (5.12) in the subspace conservation proposition with $f = -\dot{P}Tu$. Thus $\tilde{v} \in \tilde{S}(u(t))$ for all t . Now we show that equations (5.14) are conservative.

Proposition: The reduced equations (5.14) conserve $\int C^T u(t) dx$ and $C^T \tilde{v}$.

Proof. We start with $P = G(C^T G)^{-1} C^T$ and see that $C^T P = C^T G (C^T G)^{-1} C^T = C^T$. And so we use that $C^T P = C^T$ and apply this to equations (5.14).

$$\begin{aligned}\partial_t C^T u &= C^T \tilde{v} + C^T P T u = C^T \tilde{v} + C^T T u, \\ \partial_t C^T \tilde{v} &= C^T \dot{P} \tilde{v} - C^T P \dot{P} T u = C^T \dot{P} \tilde{v} - C^T \dot{P} T u.\end{aligned}\tag{5.15}$$

We differentiate $C^T P = C^T$ with respect to t to get

$$\partial_t(C^T P) = \partial_t(C^T) = 0 \implies C^T \dot{P} = 0$$

which gives us

$$\partial_t C^T u = C^T \tilde{v} + C^T T u, \quad \partial_t C^T \tilde{v} = 0.$$

This shows us that as long as $C^T \tilde{v}(0) = 0$ we have $C^T \tilde{v}(t) = 0$ for all t because $\partial_t C^T \tilde{v} = 0$. We put this into the first equation of (5.15) and get $\partial_t C^T u = C^T T u$ and so

$$\partial_t \int C^T u dx = \text{boundary terms.}$$

□

5.5 Numerical Solution of the Reduced Problem

The computation of the time derivative $\dot{P} = \frac{d}{dt} P(u(t))$ would be a quite involved numerical task and so we introduce the following notation for the numerical solution:

We replace \tilde{v} with v for notational convenience and start with

$$u(t_0), v(t_0) \text{ with } v(t_0) \in \tilde{S}(t_0) \iff v(t_0) = P(u(t_0))v(t_0).$$

Step 1: We begin with equation (5.14) and solve

$$\partial_t u = v(t_0) + P(u(t_0)) T u(t_0).$$

We use a forward Euler time step to compute $u(t_0 + h)$ and \dot{P} as follows,

$$\frac{u(t_0 + h) - u(t_0)}{h} = v(t_0) + P(u(t_0))Tu(t_0).$$

Solve for $u(t_0 + h)$

$$u(t_0 + h) = u(t_0) + h[v(t_0) + P(u(t_0))Tu(t_0)]. \quad (5.16)$$

$P(u(t_0 + h))$

$$= \frac{1}{u_1(t_0 + h) + u_2(t_0 + h)} \begin{bmatrix} u_1(t_0 + h) & -u_1(t_0 + h) & 0 \\ -u_2(t_0 + h) & u_2(t_0 + h) & 0 \\ u_2(t_0 + h) & u_1(t_0 + h) & u_1(t_0 + h) + u_2(t_0 + h) \end{bmatrix}$$

Now we introduce a new variable Q to identify the computed approximation for \dot{P} . We let $Q = \frac{1}{h} \left(P(u(t_0 + h)) - P(u(t_0)) \right) \approx \dot{P}$.

Step 2: Solve the unconstrained step.

The first order condition to find the unconstrained maximum of a function, u , is that $u' = 0$. And so we take equation (5.14) and let $\partial_t u = 0$. Now we introduce another new variable, w , to identify the unconstrained value v . So $w(0) = v(t_0)$. From equation (5.14) with $\partial_t u = 0$ we have

$$\begin{aligned} 0 = v(t_0) + PTu(t_0) &\implies \partial_t w = -QTu(t_0 + h) \\ &\implies \frac{w(0 + h) - w(0)}{h} = -QTu(t_0 + h). \end{aligned}$$

This gives us that

$$w(h) = v(t_0) - h[QTu(t_0 + h)], \quad w(0) = v(t_0). \quad (5.17)$$

Step 3: Let's review our notation. Recall that w is our computed value for v which is \tilde{v} which is in \tilde{S} which implies that $w = Pw$ where P is our projection. So we have

$$w(t_0 + h) = P(u(t_0 + h))w(t_0 + h).$$

This conserves the property $v(t_0 + h) = P(u(t_0 + h))v(t_0 + h)$.

Now we show that this scheme is order 1 consistent.

Proposition: This scheme is consistent of order 1.

Proof. A method is said to be consistent if the local truncation error goes to zero as the time step goes to zero (LeVeque (2007)). In order to prove that this scheme is consistent of order 1, we have to show that

$$u(t + h) = u(t) + hv(t) + hP(u(t))Tu(t) + O(h^2), \text{ and}$$

$$v(t + h) = v(t) + h\dot{P}(u(t))v(t) - hP(u(t))\dot{P}(u(t))Tu(t) + O(h^2).$$

We Taylor expand $u(t_0 + h)$ and substitute for $\partial_t u(t_0)$ from equation (5.14).

$$u(t_0 + h) = u(t_0) + h\partial_t u(t_0) + \frac{h^2}{2}\partial_t^2 u(t_0) + \dots$$

$$u(t_0 + h) = u(t_0) + h[v(t_0) + P(u(t_0))Tu(t_0)] + O(h^2).$$

Now we Taylor expand $v(t_0 + h)$ and substitute for $\partial_t v(t_0)$ from equation (5.14).

$$v(t_0 + h) = v(t_0) + h\partial_t v(t_0) + \frac{h^2}{2}\partial_t^2 v(t_0) + \dots$$

$$v(t_0 + h) = v(t_0) + h[\dot{P}(u(t_0))v(t_0) - P(u(t_0))\dot{P}(u(t_0))Tu(t_0)] + O(h^2).$$

Which gives us our desired result

$$u(t_0 + h) = u(t_0) + h[v(t_0) + P(u(t_0))Tu(t_0)] + O(h^2),$$

$$v(t_0 + h) = v(t_0) + h\dot{P}(u(t_0))v(t_0) - hP(u(t_0))\dot{P}(u(t_0))Tu(t_0) + O(h^2)$$

which shows that this scheme is consistent of order 1. □

Chapter 6

NUMERICAL COMPARISON

In this section we present a numerical scheme for the reduced solution and a numerical scheme for the full solution. We then propose an example problem and show the comparison of the reduced solution with the full solution.

6.1 Numerical Scheme for Reduced Solution

Given the reduced equations (5.11) which we reproduce here for convenience

$$\begin{aligned}\partial_t u &= \tilde{v} + P(u)Tu, & u(0) &= u^I, \\ \partial_t \tilde{v} &= \dot{P}(\tilde{v} + (P(u) - I)Tu), & \tilde{v}(0) &= v^I\end{aligned}\tag{6.1}$$

Step 1:

$$u(t+h) = u(t) + h[v(t) + P(u(t))Tu(t)].$$

Step 2: Compute

$$P(t+h) = P(u(t+h))$$

set

$$Q(t) \approx \dot{P} = \frac{1}{h}(P(t+h) - P(t)) \implies P(t+h) = P(t) + hQ(t) = P(t) + h\dot{P} + O(h^2).$$

Step 3: Compute the unconstrained step

$$w = v(t) + hQ(t)[v(t) + (P(t) - I)Tu(t+h)].$$

Set

$$v(t+h) = P(t+h)w$$

this guarantees $v(t) = P(t)v(t)$ for all t !

6.2 Numerical Scheme for Full Solution

We begin with equation (5.4)

$$\begin{aligned}\partial_t u &= v + Tu, & u(0) &= u^I \\ \partial_t v &= \frac{1}{\epsilon} R(u)(v + Tu), & v(0) &= v^I = \frac{1}{\epsilon} r(u^I).\end{aligned}\tag{6.2}$$

Then we have

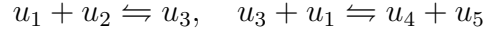
$$\begin{aligned}u(t+h) &= u(t) + h(v(t) + Tu(t)) \\ \epsilon v(t+h) &= \epsilon v(t) + h(R(u(t+h))(Tu(t+h) + v(t+h))).\end{aligned}$$

We can solve the final equation for $v(t+h)$ to get

$$\begin{aligned}u(t+h) &= u(t) + h(v(t) + Tu(t)) \\ v(t+h) &= (\epsilon I - hR(u(t+h)))^{-1}(\epsilon v(t) + h(R(u(t+h))Tu(t+h))).\end{aligned}\tag{6.3}$$

6.3 A Spatially Homogeneous Example

Let's go back to our example first introduced in Section 2.4. Given five species and two reactions as follows:



We have the following five differential equations:

$$\begin{aligned}\dot{u}_1 &= r_1 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_2 &= r_2 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\ \dot{u}_3 &= r_3 = \alpha_1^f u_1 u_2 - \alpha_1^b u_3 - \alpha_2^f u_1 u_3 + \alpha_2^b u_4 u_5 \\ \dot{u}_4 &= r_4 = \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5 \\ \dot{u}_5 &= r_5 = \alpha_2^f u_1 u_3 - \alpha_2^b u_4 u_5\end{aligned}\tag{6.4}$$

We find the jacobian $R = \frac{dr}{du}$

$$R(u) = \begin{pmatrix} -\alpha_1^f u_2 - \alpha_2^f u_3 & -\alpha_1^f u_1 & \alpha_1^b - \alpha_2^f u_1 & \alpha_2^b u_5 & \alpha_2^b u_4 \\ -\alpha_1^f u_2 & -\alpha_1^f u_1 & \alpha_1^b & 0 & 0 \\ \alpha_1^f u_2 - \alpha_2^f u_3 & \alpha_1^f u_1 & -\alpha_1^b - \alpha_2^f u_1 & \alpha_2^b u_5 & \alpha_2^b u_4 \\ \alpha_2^f u_3 & 0 & \alpha_2^f u_1 & -\alpha_2^b u_5 & -\alpha_2^b u_4 \\ \alpha_2^f u_3 & 0 & \alpha_2^f u_1 & -\alpha_2^b u_5 & -\alpha_2^b u_4 \end{pmatrix}$$

The stoichiometry matrix is:

$$S = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 \end{pmatrix}$$

A basis for the nullspace of S is

$$C = \begin{pmatrix} -1 & 1 & 1 \\ 2 & -1 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

And so we have $C^T R = 0$

Each timestep we compute a new value for R and use that to compute a new value for G which we use to find

$$P = G(C^T G)^{-1} C^T$$

We set $\alpha_1^f = 0.5$, $\alpha_1^b = 1$, $\alpha_2^f = 0.5$, and $\alpha_2^b = 1$. In accordance with our quasi-steady-state assumption, we chose values for u^I so that $r \approx \epsilon$ which we set at 1×10^{-6} . We used a stepsize of $h = 0.01$. Since the transport operator T is diagonal in the species index, and we consider a spatially homogeneous problem in this example, the

transport operator T reduces to a diagonal matrix in the species u and has non-positive eigenvalues. In this example we set the transport operator to be

$$T = \text{diag}(-2, -1.5, -1, -0.5, 0) .$$

A summary of parameters used for figure 6.1 is given in table 6.1.

Table 6.1: Parameters Used in Computing and Plotting Figure 6.1.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	0.5
Coefficient of the first backward reaction (α_1^b)	1
Coefficient of the second forward reaction (α_2^f)	0.5
Coefficient of the second backward reaction (α_2^b)	1
Separation of time scales (ϵ)	1×10^{-6}
Timestep (h)	0.01
Transport operator	$\text{diag}(-2, -1.5, -1, -0.5, 0)$

For the full solution we solved the scheme (6.3) for $t \in [0, 1] \times 10^{-4}$ and solved the reduced problem with the first order scheme explained in Section 6.1. As you can see in Figure 6.1, the solutions match very well.

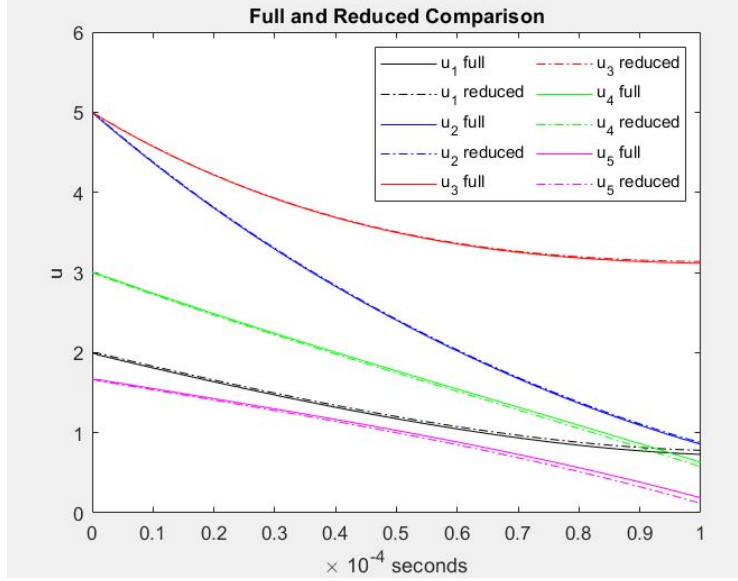
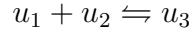


Figure 6.1: Comparison of Full Solution to Reduced Solution (Five Species and Two Reactions).

6.4 A Spatially Inhomogeneous Example

We take an example similar to the example in Appendix A. Given three species and one reversible reaction as follows:



We have the following three differential equations:

$$\begin{aligned} \dot{u}_1 &= r_1 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\ \dot{u}_2 &= r_2 = -\alpha_1^f u_1 u_2 + \alpha_1^b u_3 \\ \dot{u}_3 &= r_3 = \alpha_1^f u_1 u_2 - \alpha_1^b u_3 \end{aligned} \tag{6.5}$$

We find the jacobian $R = \frac{dr}{du}$

$$R(u) = \begin{pmatrix} -\alpha_1^f u_2 & -\alpha_1^f u_1 & \alpha_1^b \\ -\alpha_1^f u_2 & -\alpha_1^f u_1 & \alpha_1^b \\ \alpha_1^f u_2 & \alpha_1^f u_1 & -\alpha_1^b \end{pmatrix} = \Gamma \text{diag}(u_2, u_1, 1), \quad \Gamma = \begin{pmatrix} -\alpha_1^f & -\alpha_1^f & \alpha_1^b \\ -\alpha_1^f & -\alpha_1^f & \alpha_1^b \\ \alpha_1^f & \alpha_1^f & -\alpha_1^b \end{pmatrix}$$

A basis for the nullspace of R is found by first computing the basis for the nullspace of Γ as follows

$$N(\Gamma) = H = \begin{pmatrix} -1 & \alpha_1^b \\ 1 & 0 \\ 0 & \alpha_1^f \end{pmatrix}, \quad N(R) = G(u) = \text{diag}(u_2, u_1, 1)^{-1}H = \begin{pmatrix} \frac{-1}{u_2} & \frac{\alpha_1^b}{u_2} \\ \frac{-1}{u_1} & 0 \\ 0 & \alpha_1^f \end{pmatrix}$$

The stoichiometry matrix is:

$$\mathbf{S} = \begin{pmatrix} -1 & -1 & 1 \end{pmatrix}$$

A basis for the nullspace of S is

$$C = \begin{pmatrix} -1 & 1 \\ 1 & 0 \\ 0 & 1 \end{pmatrix}$$

And again we have $C^T R = 0$.

Each timestep we compute a new value for R and use that to compute a new value for H and Γ which we use to find

$$P = G(C^T G)^{-1} C^T$$

We note that the units of u are particles per cm. Therefore the units of $\dot{u} = r$ are particles per (cm \times time). Thus we have that the units of α^b are u/time or particles per (cm \times time). The units of α^f are $1/\text{time}$. We set $\alpha_1^f = 4, \alpha_1^b = 0.1$. In accordance with our quasi-steady-state assumption, we chose values for u^I so that $r \approx \epsilon$ which we set at 1×10^{-1} . We used a time stepsize of $h = 0.1$. In this case we add a one dimensional spatial variable of $x \in [0, 1]$ with a stepsize of $\Delta x = 0.05$. The transport operator T is given by equation (4.2). We set the diffusion coefficient equal to four

for each specie. We set the mobility equal to one. Since we take the electrodynamic potential to be linear, the electric field is constant and we set it equal to two. We look at two cases for the charge.

- **Case 1.** In this case we have that u_1 is a mobile atom (e.g. cadmium), u_2 is a free site, and u_3 is an atom on a fixed site on a lattice. In this case z_2 should be zero. And z_1 and z_3 should be the same, either negative one or zero. In the first case we take z_1 and z_3 to be zero. We summarize the parameters used for Case 1 in table 6.2.
- **Case 2.** In this case we have that u_1 is an electron, u_2 is an uncharged particle, and u_3 is a negative ion. In this case z_1 will be negative one, z_2 will be zero, and z_3 will be negative one. We summarize the parameters used for Case 2 in table 6.3.

Table 6.2: Parameters Used in Computing and Plotting Figure 6.2.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	4
Coefficient of the first backward reaction (α_1^b)	0.1
Separation of time scales (ϵ)	1×10^{-1}
Timestep (h)	0.1
Spatial stepsize (Δx)	0.05
Diffusion Coefficient (D)	$diag(4, 4, 4)$
Mobility (μ)	$diag(1, 1, 1)$
Electric Field ($\nabla_x V$)	4
Charge (z)	$diag(0, 0, 0)$

Table 6.3: Parameters Used in Computing and Plotting Figure 6.3.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	4
Coefficient of the first backward reaction (α_1^b)	0.1
Separation of time scales (ϵ)	1×10^{-1}
Timestep (h)	0.1
Spatial stepsize (Δx)	0.05
Diffusion Coefficient (D)	$diag(4, 4, 4)$
Mobility (μ)	$diag(1, 1, 1)$
Electric Field ($\nabla_x V$)	4
Charge (z)	$diag(-1, 0, -1)$

For the full solution we solved the scheme (6.3) for $t \in [0, 20] \times 10^{-4}$ and solved the reduced problem with the first order scheme explained in Section 6.1. In Figures 6.2 and 6.3, we show the results of the full and reduced solutions for cases one and two at $x = 0.25$ microns, $x = 0.55$ microns, and $x = 0.85$ microns. As you can see in these figures, the solutions match very well. We computed the norm of the difference of the full and reduced solutions over the norm of the full solution at the last time step. We got 0.0124 for case one and 0.0057 for case two.

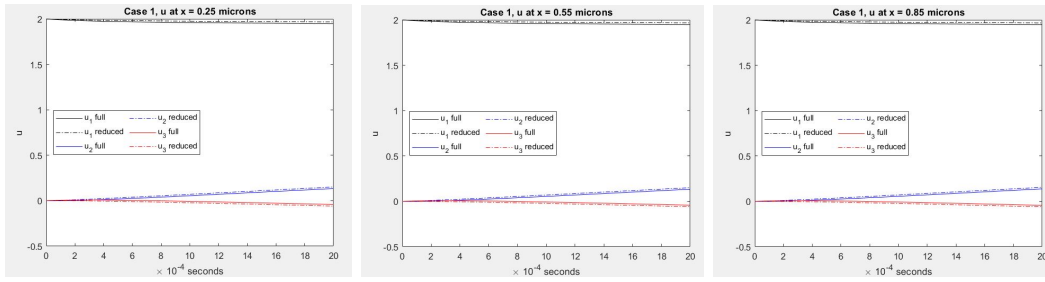


Figure 6.2: Case 1 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.

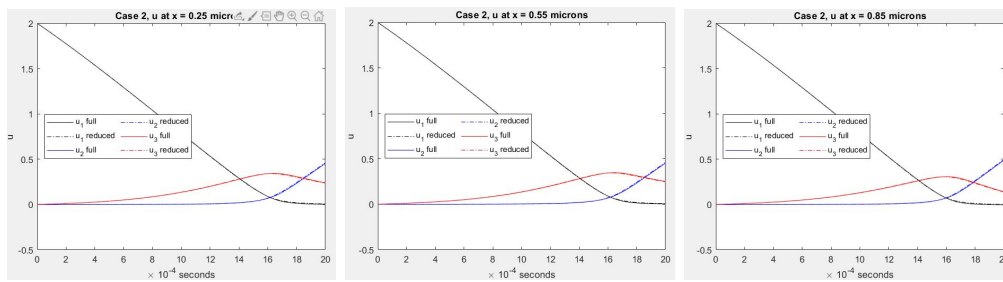


Figure 6.3: Case 2 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.

OPERATOR SPLITTING METHODS

Operator splitting is a numerical method of computing the solution of a differential equation. The splitting method separates the original equation into two parts over a single time step, separately computes the solution to each part, and then combines the two separate solutions to form a solution to the original equation (MacNamara and Strang (2016)). We apply operator splitting techniques (MacNamara and Strang (2016), Sportisse (2000)). The systems under consideration are of stiff type, which Sportisse addresses in his paper. In practical applications the use of operator splitting methods is a necessity to keep the computational cost within reasonable bounds. The goal of the work in Chapter 7 is to develop a numerical method that is a consistent solver for the original reaction transport system, which implicitly solves the reduced problem for time steps chosen much larger than the time scale of the fastest reactions. We demonstrate the necessity for operator splitting methods in Section 7.1 by comparing computational costs of a fully implicit scheme with the cost of separating the transport and the reaction parts of the equations by operator splitting. We give an overview of existing theory in Section 7.3.

7.1 Reasons

For realistic systems of the form (5.1), it is imperative to use operator splitting methods, separating the reaction term, r , and the transport operator, T . In the following we give a rough reasoning for this statement using operation counts under simplified assumptions. The actual operation count will depend on the actual numerical method used. However, the basic conclusion will still hold. Namely, that for a

realistic reaction diffusion system with $O(50)$ species in two spatial dimensions, the use of operator splitting is imperative. An operator splitting method for the system (5.1) would be of the following form. Given $u(t)$ and time step h , compute $u(t+h)$ by solving reaction and spatial transport separately.

- Step 1: The reaction step. Solve

$$\partial_t w_1 = \frac{1}{\epsilon} r(w_1), \quad w_1(t) = u(t), \quad \text{set } u_1 = w_1(t+h).$$

- Step 2: The transport step. Solve

$$\partial_t w_2 = T w_2, \quad w_2(t) = u_1, \quad \text{set } u(t+h) = w_2(t+h).$$

We compare this to a direct solution of the system (5.1). Since the original system (5.1) is stiff in time we would have to use an implicit time discretization method for the full system to be able to use time steps on the order of the slow reactions. We compare the computational cost of an implicit method for the full system with the cost of an operator splitting method. For simplicity, let us assume that the involved nonlinear equations at each implicit time step are solved by a Newton type algorithm and that the resulting linear equations are solved by a direct sparse solver. We restrict this comparison to the case of simulations in two spatial dimensions, since one spatial dimension is, in general, not enough to represent the transport mechanisms in a solar cell and nobody would use a direct solver in three spatial dimensions. The computational work for a direct sparse solution of a system of M equations with a matrix bandwidth b is roughly given by $O(Mb^2)$. Considering a reaction diffusion system with N species and $O(K^2)$ grid points (or finite element cells) in two dimensions we have roughly $M = NK^2$ and $b = NK$, giving a computational cost of $O(N^3K^4)$ operations per linear solve for a straightforward use of an implicit method for the full system (5.1). Comparing this to the cost of the operator splitting method,

we have to solve K non-linear equations which will take K^2 operations, involving N^3 operations per Newton step for the (full) linear systems, giving $O(K^2N^3)$ operations for Step 1. In Step 2 we solve N separate two-dimensional transport equations. Each of these equations gives a $K^2 \times K^2$ system with a matrix bandwidth K , and therefore involves $O(K^4)$ operations. All together, the operation count for the operator splitting method per linear solve is $O(N^3K^2 + NK^4)$ whereas the operation count for the direct solution per linear solve would be $O(N^3K^4)$. This gives a ratio of

$$\frac{\text{direct}}{\text{operator splitting}} = \frac{N^2K^2}{N^2 + K^2}.$$

For realistic numbers ($N = O(50)$, $K = O(100)$), this gives a speedup factor of roughly 1000 of the operator splitting method over the direct solution.

This is a very rough comparison only. The performance of the direct solver could be improved, even in two dimensions, using iterative solvers for the involved linear systems, but so could the performance of the operator splitting solver in Step 2. On the other hand, this comparison assumes operation counts on a purely linear machine, not taking into account parallelization. Parallelization, or vectorization, will actually work in favor of the operator splitting method. So, in summary, to make the solution of the reaction-transport system (5.1) feasible on a standard desktop-type computer, for realistic values of the number of species and gridpoints, it is necessary to employ the operator splitting method.

7.2 Self Consistent Potentials and Gummel's Algorithm

To include a self consistent potential V into the simulation, Poisson's equation (4.3) has to be solved dynamically together with the reaction and the transport equations. This will couple the transport step in the operator splitting method across the

species index n as well as across the spatial variable x . The standard approach to deal with this problem is an iterative method, commonly known as Gummel iteration (Selberherr (1984)), which adds an inner loop to the operator splitting method in Section 7.1 to resolve the resulting nonlinearity.

Remark: The operator splitting algorithm presented in this section will still suffer from a severe restriction on the time step $h = t_{k+1} - t_k$, due to the stiffness of the problem for $\epsilon \ll 1$ (Sportisse (2000)). The purpose of this section is to show that, using Gummel's algorithm, the inclusion of a self consistent potential V via the Poisson equation (7.1) is just an add-on to the operator splitting method, involving an additional inner loop for Gummel's iteration. An asymptotically preserving operator splitting method, based on the asymptotic analysis in Chapter 5, avoiding the restriction on the time step due to the stiffness, will be discussed in Chapter 8.

An alternate discussion of Gummel's method is given in Appendix B. Given the system of transport equations $\partial_t \vec{u} = \vec{T}$, where the nonlinear operator \vec{T} is given by (4.2) as

$$\vec{T} = (T_1, \dots, T_n), \quad T_n(\vec{u}) = \nabla_x \cdot [D_n \nabla_x u_n + z_n \mu_n u_n \nabla_x V]$$

and the potential $V = V(\vec{u})$ is given by the Poisson equation (4.3)

$$-\nabla_x \cdot (\kappa \nabla_x V) = \sum_{n=1}^N z_n u_n + D, \quad (7.1)$$

Gummel's method (Selberherr (1984)) consists of iterating between the Poisson equation (4.3) and the transport equation system (4.2) after using the variable transfor-

mation $u_n = e^{\frac{-z_n \mu_n}{D_n}} s_n, n = 1 : N$ resulting in the system

$$(a) -\nabla_x \cdot (\kappa \nabla_x V) = \sum_{n=1}^N z_n e^{\frac{-z_n \mu_n}{D_n} V} s_n + D \quad (7.2)$$

$$(b) \partial_t (e^{\frac{-z_n \mu_n}{D_n} V} s_n) = \nabla_x \cdot (D_n e^{\frac{-z_n \mu_n}{D_n} V} \nabla_x s_n), \quad n = 1 : N .$$

The transformed variables s_n are often referred to as Slotboom variables (Vook *et al.* (2000)) in the engineering literature. Gummel's algorithm now consists of iterating between (7.2) (a) and (7.2) (b) until convergence is reached, i.e. solving iteratively

$$(a) -\nabla_x \cdot (\kappa \nabla_x V^j) = \sum_{n=1}^N z_n e^{\frac{-z_n \mu_n}{D_n} V^j} s_n^{j-1} + D \quad (7.3)$$

$$(b) \partial_t (e^{\frac{-z_n \mu_n}{D_n} V^j} s_n^j) = \nabla_x \cdot (D_n e^{\frac{-z_n \mu_n}{D_n} V^j} \nabla_x s_n^j), \quad n = 1 : N ,$$

$j = 1, 2, \dots$, thus transferring the nonlinearity in the system (7.2) from the transport equations (7.2) (b) to the, now nonlinear, Poisson equation (7.3) (a) within the iteration. After reverting to the original densities, given by $u_n = e^{\frac{-z_n \mu_n}{D_n}} s_n, n = 1 : N$, (7.3) becomes

$$(a) -\nabla_x \cdot (\kappa \nabla_x V^j) = \sum_{n=1}^N z_n e^{\frac{z_n \mu_n}{D_n} (V^{j-1} - V^j)} u_n^{j-1} + D \quad (7.4)$$

$$(b) \partial_t u_n^j = T_n [V^j] u_n^j = \nabla_x \cdot [D_n \nabla_x u_n^j + z_n \mu_n u_n^j \nabla_x V^j], \quad n = 1 : N .$$

So, for an iterate V^j , computed from (7.4) (a), equation (7.4) (b) becomes linear in u^j . More importantly, equation (7.4) (b) can be solved separately for each species u_n , regaining the advantages of the operator splitting methods outlined in Section 7.1. The modification of the operator splitting method in Section 7.1, including the nonlinear coupling of the species through the self consistent potential V , is now of the form: Given $V(x, t_k)$ and $\vec{u}(x, t_k)$:

- Step 1: The reaction step. Solve

$$\partial_t \vec{w} = \frac{1}{\epsilon} \vec{r}(\vec{w}), \quad t_k < t < t_{k+1}, \quad \vec{w}(x, t_k) = \vec{u}(x, t_k), \quad \text{set } \vec{u}^{(1)}(x) = \vec{w}(x, t_{k+1}),$$

with $\vec{w} = (w_1, \dots, w_N)$, $\vec{r} = (r_1, \dots, r_N)$

- Step 2: The (nonlinear) transport step. Starting with $V^0(x, t) = V(x, t_k)$, $\vec{w}^0(x, t_k) = \vec{u}^{(1)}(x)$,

- Step 2(a): Solve $-\nabla_x \cdot (\kappa \nabla_x V^j) = \sum_{n=1}^N z_n e^{\frac{z_n \mu_n}{D_n} (V^{j-1} - V^j)} w_n^{j-1} + D$,

- Step 2(b): Solve $\partial_t \vec{w}^j = \vec{T}[V^j] \vec{w}^j$, $\vec{w}^j(x, t_k) = \vec{u}^{(1)}(x)$, for $t_k < t < t_{k+1}$ and $j = 1, 2, \dots$

- Step 3: Upon convergence of Step 2 with $\vec{w} \rightarrow \vec{w}^\infty$ and $V^j \rightarrow V^\infty$, set

$$\vec{u}(x, t_{k+1}) = \vec{w}^\infty(x, t_{k+1}), \quad V(x, t_{k+1}) = V^\infty(x, t_{k+1})$$

Remark: The above operator splitting algorithm retains the advantage of the operator splitting method, namely that Step 2(b) can be carried out separately for each species $n = 1 : N$, once V^j has been computed from Step 2(a).

7.3 General Convergence Theory for Operator Splitting Methods

We will begin with an ODE example (MacNamara and Strang (2016)).

$$\frac{du}{dt} = (A + B)u$$

whose solution is

$$u(h) = u(0)e^{h(A+B)}$$

which looks pretty easy to compute. But what if it isn't easy? What if we can compute e^{hA} and e^{hB} separately but not $e^{h(A+B)}$? A first order splitting approximation would be

$$e^{h(A+B)} \approx e^{hA}e^{hB}. \tag{7.5}$$

Let's take the case where A and B are matrices and show why this is only a first order approximation. We start with a Taylor series expansion of each term.

$$e^{h(A+B)} = I + h(A+B) + \frac{h^2}{2}(A+B)^2 + \frac{h^3}{6}(A+B)^3 + \dots$$

$$e^{hA} = I + hA + \frac{h^2}{2}A^2 + \frac{h^3}{6}A^3 + \dots$$

$$e^{hB} = I + hB + \frac{h^2}{2}B^2 + \frac{h^3}{6}B^3 + \dots$$

Now we put this into equation (7.5) to see

$$I + h(A+B) + \frac{h^2}{2}(A+B)^2 + O(h^3)$$

$$= \left(I + hA + \frac{h^2}{2}A^2 + O(h^3) \right) \left(I + hB + \frac{h^2}{2}B^2 + O(h^3) \right)$$

Now we do the multiplication on the right hand side (RHS)

$$\text{RHS} = I + hA + \frac{h^2}{2}A^2 + hB + h^2AB + \frac{h^2}{2}B^2 + O(h^3)$$

We rearrange terms and see

$$\text{RHS} = I + h(A+B) + \frac{h^2}{2}(A^2 + 2AB + B^2) + O(h^3)$$

This gives us

$$I + h(A+B) + \frac{h^2}{2}(A+B)^2 + O(h^3) = I + h(A+B) + \frac{h^2}{2}(A^2 + 2AB + B^2) + O(h^3).$$

The 2nd order terms don't always match because

$$(A+B)^2 = (A^2 + 2AB + B^2)$$

only when the matrices commute. Therefore, equation (7.5) is only a first order approximation unless the matrices A and B commute.

The symmetric Strang splitting is presented in MacNamara and Strang (MacNamara and Strang (2016)) as follows

$$e^{h(A+B)} \approx e^{\frac{h}{2}A} e^{hB} e^{\frac{h}{2}A}. \quad (7.6)$$

This is second order splitting. To illustrate this, we proceed as above with Taylor series expansion of each term

$$e^{h(A+B)} = I + h(A+B) + \frac{h^2}{2}(A+B)^2 + \frac{h^3}{6}(A+B)^3 + \dots$$

$$e^{\frac{h}{2}A} = I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + \dots$$

$$e^{hB} = I + hB + \frac{h^2}{2}B^2 + \frac{h^3}{6}B^3 + \dots$$

Now we put this into equation (7.6)

$$\begin{aligned} I + h(A+B) + \frac{h^2}{2}(A+B)^2 + \frac{h^3}{6}(A+B)^3 + \dots &= \left(I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + \dots \right) \\ &\quad \left(I + hB + \frac{h^2}{2}B^2 + \frac{h^3}{6}B^3 + \dots \right) \left(I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + \dots \right) \end{aligned} \quad (7.7)$$

We multiply the square and cube on the left hand side (LHS)

$$\frac{h^2}{2}(A+B)^2 = \frac{h^2}{2}(A^2 + AB + BA + B^2)$$

$$\frac{h^3}{6}(A+B)^3 = \frac{h^3}{6}(A^3 + ABA + BA^2 + B^2A + A^2B + AB^2 + BAB + B^3)$$

We put this back into the LHS of Equation (7.7) to get

$$\begin{aligned} \text{LHS} &= I + h(A+B) + \frac{h^2}{2}(A^2 + AB + BA + B^2) \\ &\quad + \frac{h^3}{6}(A^3 + ABA + BA^2 + B^2A + A^2B + AB^2 + BAB + B^3) + O(h^4) \end{aligned} \quad (7.8)$$

Now we start on the RHS by multiplying the first two terms

$$\left(I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + \dots \right) \left(I + hB + \frac{h^2}{2}B^2 + \frac{h^3}{6}B^3 + \dots \right)$$

$$= I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + hB + \frac{h^2}{2}AB + \frac{h^3}{8}A^2B + \frac{h^2}{2}B^2 + \frac{h^3}{4}AB^2 + \frac{h^3}{6}B^3 + O(h^4)$$

We multiply this with the last term on the RHS

$$\begin{aligned} & \left(I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + hB + \frac{h^2}{2}AB + \frac{h^3}{8}A^2B + \frac{h^2}{2}B^2 + \frac{h^3}{4}AB^2 + \frac{h^3}{6}B^3 \right. \\ & \quad \left. + O(h^4) \right) \left(I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + \dots \right) \\ & = I + \frac{h}{2}A + \frac{h^2}{8}A^2 + \frac{h^3}{48}A^3 + hB + \frac{h^2}{2}AB + \frac{h^3}{8}A^2B + \frac{h^2}{2}B^2 \\ & + \frac{h^3}{4}AB^2 + \frac{h^3}{6}B^3 + \frac{h}{2}A + \frac{h^2}{4}A^2 + \frac{h^3}{16}A^3 + \frac{h^2}{2}BA + \frac{h^3}{4}ABA + \frac{h^3}{4}B^2A + \frac{h^2}{8}A^2 + \frac{h^3}{16}A^3 \\ & \quad + \frac{h^3}{8}BA^2 + \frac{h^3}{48}A^3 + O(h^4) \end{aligned}$$

Combining like terms we get

$$\begin{aligned} \text{RHS} & = I + h(A + B) + \frac{h^2}{2}(A^2 + AB + BA + B^2) \\ & + \frac{h^3}{6} \left(A^3 + \frac{3}{4}A^2B + \frac{3}{2}AB^2 + \frac{3}{2}ABA + \frac{3}{2}B^2A + \frac{3}{4}BA^2 + B^3 \right) + O(h^4) \end{aligned} \quad (7.9)$$

We look at the local error by subtracting Equation (7.8) from Equation (7.9). We notice that I and the h and h^2 terms cancel, and we are left with

$$\begin{aligned} \text{local error} & = \frac{h^3}{6} \left(A^3 + \frac{3}{4}A^2B + \frac{3}{2}AB^2 + \frac{3}{2}ABA + \frac{3}{2}B^2A + \frac{3}{4}BA^2 + B^3 \right) \\ & - \frac{h^3}{6} (A^3 + ABA + BA^2 + B^2A + A^2B + AB^2 + BAB + B^3) + O(h^4) \\ & = \frac{h^3}{6} \left(\frac{1}{2}ABA - \frac{1}{4}BA^2 + \frac{1}{2}B^2A - \frac{1}{4}A^2B + \frac{1}{2}AB^2 - BAB \right) + O(h^4) \end{aligned}$$

So we see that

$$\text{local error} = Ch^3 + O(h^4)$$

Where the constant C is given by

$$C = \frac{1}{24} (2ABA - BA^2 + 2B^2A - A^2B + 2AB^2 - 4BAB)$$

If we define a difference operator by $[A, B] = AB - BA$ then we can show that

$$C = \frac{1}{24} ([[A, B], A] + 2[[A, B], B])$$

Proof.

$$\begin{aligned} C &= \frac{1}{24} ([(AB - BA), A] + 2[(AB - BA), B]) \\ &= \frac{1}{24} ((ABA - BAA - AAB + ABA) + 2(ABB - BAB - BAB + BBA)) \\ &= \frac{1}{24} (2ABA - BAA - AAB + 2ABB - 4BAB + 2BBA) \end{aligned}$$

Which is our desired result. □

We note that second order operator splitting introduces an error which cancels out the benefits (MacNamara and Strang (2016)) therefore in this work we use a first order splitting method.

ASYMPTOTICALLY PRESERVING SCHEMES

The basic idea of asymptotically preserving methods is the following: Consider a problem depending on a small parameter ϵ . Consider the discretization of this problem depending on a small parameter h (a stepsize). There are two iterated limits to be considered

- The limit $h \rightarrow 0, \epsilon \rightarrow 0$, giving the continuous solution of the full problem first (if the scheme is convergent) and then the solution of the reduced problem for $\epsilon \rightarrow 0$.
- The limit $\epsilon \rightarrow 0, h \rightarrow 0$, giving the continuous solution of the limiting solution of the discretization for $\epsilon \rightarrow 0$ first, and then the continuum limit of this limiting solution for $h \rightarrow 0$.

The definition of an asymptotically preserving scheme is that these two limits commute. This means in practice that we get the same solution for $\epsilon \ll h$ and $h \ll \epsilon$. Therefore we can take large time steps $h \gg \epsilon$ and still compute the correct solution on large time scales.

In this section we address asymptotically preserving methods and their applications to modeling the efficiency and lifetime of solar cells. We will also present a proof that L-stable methods are asymptotically preserving for the reaction diffusion system.

8.1 An Asymptotically Preserving Scheme

Based on the asymptotic analysis developed in Chapter 5, we develop and implement an asymptotically preserving scheme that allows us to compute the solutions efficiently (on the transport time scale). We briefly outline the basic idea here. Since the asymptotically preserving scheme must reflect the properties of the limiting asymptotic solution in Chapter 5 we discretize the original problem in the formulation (5.4), using the reaction product $v = \frac{1}{\epsilon}r(u)$ as an additional variable. We consider the system

$$\begin{aligned} \partial_t u &= v + Tu, \\ \epsilon \partial_t v &= R(u)(v + Tu). \end{aligned} \tag{8.1}$$

In addition, we have to discretize this system by an operator splitting method, treating transport and reactions separately, for the reasons of computational efficiency outlined in Section 7.1. There are various ways to achieve this goal. One possible way would be the following scheme: given $u(t_n)$ and $v(t_n)$, compute $u(t_{n+1})$ and $v(t_{n+1})$.

- Step 1: solve

$$\begin{aligned} (a) \quad \partial_t u_1 &= Tu_1, \quad u_1(t_n) = u(t_n), \\ (b) \quad \epsilon \partial_t v_1 &= R(u_1)(v_1 + Tu_1), \quad v_1(t_n) = v(t_n). \end{aligned} \tag{8.2}$$

for $t_n < t < t_{n+1} = t_n + \Delta t$

- Step 2: solve

$$\begin{aligned} (a) \quad \partial_t u_2 &= v_2, \quad u_2(t_n) = u_1(t_{n+1}), \\ (b) \quad \epsilon \partial_t v_2 &= 0, \quad v_2(t_n) = v_1(t_{n+1}) \end{aligned} \tag{8.3}$$

for $t_n < t < t_{n+1} = t_n + \Delta t$

- Step 3: set

$$u(t + \Delta t) = u_2(t + \Delta t) ,$$

$$v(t + \Delta t) = v_2(t + \Delta t) .$$

Note that this method has essentially the same advantages in terms of computational costs as outlined in Section 7.1. Step 1(a) can be performed separately for each species. In Step 1(b) the variables $u_1(t)$ and $Tu_1(t)$ are known inhomogeneous terms, and Step 1(b) can be performed for each gridpoint (or finite element) separately. Step 2 is just a simple integration. In the following we prove that the scheme above is actually asymptotically stable and verify this on computation ALT tests for more realistic problems.

8.2 AP Applied to the Full Solution

We apply this Asymptotically Preserving (AP) scheme to the full solution presented in Chapter 6. We again begin with equation (5.4)

$$\begin{aligned} (a) \quad \partial_t u &= v + Tu, \quad u(0) = u^I \\ (b) \quad \partial_t v &= \frac{1}{\epsilon} R(u)(v + Tu), \quad v(0) = v^I = \frac{1}{\epsilon} r(u^I). \end{aligned} \tag{8.4}$$

- Step 1: Solve

$$(a) \quad \partial_t u_1 = Tu_1, \quad u_1(t_n) = u(t_n),$$

$$(b) \quad \epsilon \partial_t v_1 = R(u_1)(v_1 + Tu_1), \quad v_1(t_n) = v(t_n)$$

Then we have

$$u_1(t + h) = u_1(t) + hTu(t + h)$$

$$\epsilon v_1(t + h) = \epsilon v_1(t) + h(R(u_1(t + h))(Tu_1(t + h) + v_1(t + h))).$$

We solve the first equation for $u_1(t+h)$ and the second equation for $v_1(t+h)$ to get

$$\begin{aligned} u_1(t+h) &= (I - hT)^{-1}u_1(t) \\ v_1(t+h) &= (\epsilon I - hR(u_1(t+h)))^{-1}(\epsilon v_1(t) + h(R(u_1(t+h))Tu_1(t+h))). \end{aligned} \tag{8.5}$$

for $t_n < t < t_{n+1} = t_n + h$

- Step 2: Solve

$$\begin{aligned} (a) \quad \partial_t u_2 &= v_2, \quad u_2(t_n) = u_1(t_{n+1}), \\ (b) \quad \epsilon \partial_t v_2 &= 0, \quad v_2(t_n) = v_1(t_{n+1}) \end{aligned}$$

Then we have

$$\begin{aligned} u_2(t+h) &= u_2(t) + h(v_1(t+h)) \\ v_2(t+h) &= v_2(t) = v_1(t+h). \end{aligned} \tag{8.6}$$

for $t_n < t < t_{n+1} = t_n + h$

- Step 3: Set

$$\begin{aligned} u(t+h) &= u_2(t+h) \\ v(t+h) &= v_2(t+h). \end{aligned} \tag{8.7}$$

8.3 AP Applied to the Reduced Solution

We begin with an analysis of the asymptotically preserving scheme on the reduced equations ($\epsilon = 0$). We proceed as in section 5.3. We split v into the part that is in the nullspace of R and the part that is in the orthogonal complement of the nullspace of R with $v = \tilde{v} + \hat{v}$ with $\tilde{v} = P(u)v$ and $\hat{v} = (I - P(u))v$. We recall that $\dot{P} = \frac{d}{dt}P(u(t))$.

We differentiate \tilde{v}_1 with respect to t and then substitute in for $\partial_t v_1$ from equation (8.2) (b) as follows

$$\begin{aligned}\partial_t \tilde{v}_1 &= \partial_t(Pv_1) = \dot{P}v_1 + P\partial_t v_1 \\ &= \dot{P}v_1 + P\left(\frac{1}{\epsilon}\right)R(v_1 + Tu_1) = \dot{P}v_1.\end{aligned}$$

Here we have used that $PR = 0$

Now we differentiate \hat{v}_1 with respect to t and then substitute in for $\partial_t v_1$ from equation (8.2) (b) again

$$\begin{aligned}\partial_t \hat{v}_1 &= \partial_t(I - P)v_1 = -\dot{P}v_1 + (I - P)\partial_t v_1 \\ &= -\dot{P}v_1 + (I - P)\left(\frac{1}{\epsilon}\right)R(v_1 + Tu_1) \\ &= -\dot{P}v_1 + \left(\frac{1}{\epsilon}\right)R(v_1 + Tu_1).\end{aligned}$$

For Step 1 we have

$$\begin{aligned}\partial_t u_1 &= Tu_1, \quad u_1(0) = u^I \\ \partial_t \tilde{v}_1 &= \dot{P}(\tilde{v}_1 + \hat{v}_1), \quad \tilde{v}_1(0) = v^I \\ \partial_t \hat{v}_1 &= \left(\frac{1}{\epsilon}\right)R(\hat{v}_1 + Tu_1) - \dot{P}(\tilde{v}_1 + \hat{v}_1), \quad \hat{v}_1(0) = v^I.\end{aligned}\tag{8.8}$$

For Step 2, we use the same process as above except that we substitute from equation (8.3) (b) as follows

$$\begin{aligned}\partial_t \tilde{v}_2 &= \partial_t(Pv_2) = \dot{P}v_2 + P\partial_t v_2 = \dot{P}v_2 + P \cdot 0 = \dot{P}v_2. \\ \partial_t \hat{v}_2 &= \partial_t(I - P)v_2 = -\dot{P}v_2 + (I - P)\partial_t v_2 = -\dot{P}v_2.\end{aligned}$$

For Step 2 we have

$$\begin{aligned}\partial_t u_2 &= (\tilde{v}_2 + \hat{v}_2) \\ \partial_t \tilde{v}_2 &= \dot{P}(\tilde{v}_2 + \hat{v}_2) \\ \partial_t \hat{v}_2 &= -\dot{P}(\tilde{v}_2 + \hat{v}_2),\end{aligned}\tag{8.9}$$

Now we look for the asymptotic solution to this system of partial differential equations. We begin with Step 1 and multiply the equation for \hat{v}_1 in (8.8) by ϵ and let $\epsilon \rightarrow 0$ to find the order-one equation for \hat{v}_1 .

$$\begin{aligned}\epsilon \partial_t \hat{v}_1 &= R(\hat{v}_1 + Tu_1) - \epsilon \dot{P}(\tilde{v}_1 + \hat{v}_1), \quad (\epsilon \rightarrow 0) \\ \implies R(\hat{v}_1 + Tu_1) &= 0\end{aligned}$$

We found in section 5.3 that the solution of $R(\hat{v} + Tu) = 0$ is given by $\hat{v} = (P - I)Tu$. We apply this to \hat{v}_1 and u_1 . Now for Step 1, equation (8.8) becomes

$$\begin{aligned}\partial_t u_1 &= Tu_1, \quad u_1(0) = u^I \\ \partial_t \tilde{v}_1 &= \dot{P}(\tilde{v}_1 + (P - I)Tu_1), \quad \tilde{v}_1(0) = v^I.\end{aligned}\tag{8.10}$$

The equations for Step 2 remain as in (8.9).

This gives us the following for the numerical discretization for Step 1 and Step 2

- Step 1

$$\begin{aligned}u_1(t+h) &= (I - hT)^{-1}u_1(t) \\ \tilde{v}_1(t+h) &= (I - h\dot{P})^{-1}[\tilde{v}_1(t) + (P - I)Tu_1(t+h)].\end{aligned}\tag{8.11}$$

- Step 2

$$\begin{aligned}\tilde{v}_2(t+h) &= (I - h\dot{P})^{-1}[\tilde{v}_2(t) + h\dot{P}\hat{v}_2(t)] \\ \hat{v}_2(t+h) &= (I + h\dot{P})^{-1}[\hat{v}_2(t) - h\dot{P}\tilde{v}_2(t+h)] \\ u_2(t+h) &= u_2(t) + h[\tilde{v}_2(t+h) + \hat{v}_2(t+h)].\end{aligned}\tag{8.12}$$

8.4 Reduced Equations

We begin with a version of our asymptotically preserving scheme introduced in section 8.1. For notational purposes we will use the following:

$$\begin{aligned} u_0 &= u(t) \\ v_0 &= v(t) \\ u_2 &\approx u(t+h) \\ v_2 &\approx v(t+h) \end{aligned}$$

We will reserve u_1 and v_1 for the intermediate part (Step 1) of each time step. We discretize Step 1 from equation (8.2) and Step 2 from equation (8.3)

Step 1

$$\begin{aligned} a) \quad (I - hT)u_1 &= u_0 \quad \text{or} \quad u_1 = u_0 + hTu_1. \\ b) \quad \epsilon v_1 &= \epsilon v_0 + hR_0(Tu_1 + v_1) \quad \text{where} \quad R(u_0) = R_0 \quad \text{and} \quad RP = PR = 0. \end{aligned} \tag{8.13}$$

Step 2

$$\begin{aligned} a) \quad u_2 &= u_1 + hv_2 \\ b) \quad v_2 &= v_1 \end{aligned} \tag{8.14}$$

Step 3

$$\begin{aligned} a) \quad u(t+h) &\approx u_2 \\ b) \quad v(t+h) &\approx v_2 \end{aligned} \tag{8.15}$$

Now we split spaces in S_0 as in section 5.4, letting

$$\begin{aligned} v_0 &= \tilde{v}_0 + \hat{v}_0 \quad \text{with} \quad \tilde{v}_0 = P_0 v_0 \quad \text{and} \quad \hat{v}_0 = (I - P_0)v_0 \\ v_1 &= \tilde{v}_1 + \hat{v}_1 \quad \text{with} \quad \tilde{v}_1 = P_0 v_1 \quad \text{and} \quad \hat{v}_1 = (I - P_0)v_1 \\ \tilde{v}_0, \tilde{v}_1 &\in \tilde{S}_0 \quad \text{and} \quad \hat{v}_0, \hat{v}_1 \in \hat{S}_0 \end{aligned}$$

We split Step 1 equation b) into the following two equations using $\tilde{v}_1 = P_0 v_1$ and $\hat{v}_1 = (I - P_0)v_1$.

$$\begin{aligned}\epsilon \tilde{v}_1 &= \epsilon P_0 v_0 + h P_0 R_0 (T u_1 + v_1) \\ \epsilon \hat{v}_1 &= \epsilon (I - P_0) v_0 + h (I - P_0) R_0 (T u_1 + \tilde{v}_1 + \hat{v}_1)\end{aligned}\tag{8.16}$$

We use the fact that $\tilde{v}_0 = P_0 v_0$ and that $PR = RP = 0$ to get

$$\begin{aligned}\tilde{v}_1 &= \tilde{v}_0 \\ \epsilon \hat{v}_1 &= \epsilon \hat{v}_0 + h R_0 (T u_1 + \hat{v}_1)\end{aligned}\tag{8.17}$$

We also split Step 2 equation b) which gives us the following equations for Step 1 and Step 2

Step 1

$$\begin{aligned}a) \quad u_1 &= u_0 + h T u_1. \\ b) \quad \tilde{v}_1 &= \tilde{v}_0, \quad \epsilon \hat{v}_1 = \epsilon \hat{v}_0 + h R_0 (T u_1 + \hat{v}_1)\end{aligned}\tag{8.18}$$

Step 2

$$\begin{aligned}a) \quad u_2 &= u_1 + h v_1 \\ b) \quad \tilde{v}_2 &= P_2 v_1, \quad \hat{v}_2 = (I - P_2) v_1.\end{aligned}\tag{8.19}$$

Now we let $\epsilon \rightarrow 0$ and get the following for Step 1 b)

$$\tilde{v}_1 = \tilde{v}_0, \quad 0 = R_0 (T u_1 + \hat{v}_1)$$

We again use the first law of linear algebra to find that $\hat{v}_1 = -(I - P_0) T u_1$ and so our equations become

Step 1

$$\begin{aligned}a) \quad u_1 &= u_0 + h T u_1. \\ b) \quad \tilde{v}_1 &= \tilde{v}_0, \quad \hat{v}_1 = -(I - P_0) T u_1\end{aligned}\tag{8.20}$$

Step 2

$$\begin{aligned} a) \quad u_2 &= u_1 + hv_1 \\ b) \quad \tilde{v}_2 &= P_2 v_1, \quad \hat{v}_2 = (I - P_2)v_1. \end{aligned} \tag{8.21}$$

Now we expand up to $O(h^2)$:

Step 1 a)

$$u_1 = u_0 + hTu_1 \implies u_1 = u_0 + hT[u_0 + hTu_1] \implies u_1 = u_0 + hTu_0 + O(h^2)$$

Step 1 b)

$$\hat{v}_1 = -(I - P_0)Tu_1 \implies \hat{v}_1 = -(I - P_0)T[u_0 + hTu_1] \implies \hat{v}_1 = -(I - P_0)Tu_0 + O(h)$$

Step 2 a)

$$u_2 = u_1 + h\tilde{v}_1 + h\hat{v}_1$$

Step 2 b)

$$\begin{aligned} \tilde{v}_2 &= P_0(\tilde{v}_1 + \hat{v}_1) + h\Delta P_0(\tilde{v}_1 + \hat{v}_1) + O(h^2) \\ \hat{v}_2 &= (I - P_0)(\tilde{v}_1 + \hat{v}_1) - h\Delta P_0(\tilde{v}_1 + \hat{v}_1) + O(h^2) \end{aligned}$$

Now we eliminate u_1 , \tilde{v}_1 , and \hat{v}_1 from Step 2 up to $O(h^2)$ using Step 1 equations

Step 2 a)

$$u_2 = u_0 + hTu_0 + h\tilde{v}_0 - h(I - P_0)Tu_0 + O(h^2) = u_0 + hP_0Tu_0 + h\tilde{v}_0 + O(h^2)$$

Step 2 b)

$$\begin{aligned} \tilde{v}_2 &= \tilde{v}_0 + h\Delta P_0(\tilde{v}_0 - (I - P_0)Tu_0) + O(h^2) \\ \hat{v}_2 &= (I - P_0)(\tilde{v}_0 - (I - P_0)Tu_0) - h\Delta P_0(\tilde{v}_0 - (I - P_0)Tu_0) + O(h) \end{aligned}$$

$$\hat{v}_2 = -(I - P_0)Tu_0 + O(h)$$

Which gives us the following

Step 2

$$\begin{aligned} a) \quad u_2 &= u_0 + hP_0Tu_0 + h\tilde{v}_0 + O(h^2) \\ b) \quad \tilde{v}_2 &= \tilde{v}_0 + h\Delta P_0(\tilde{v}_0 - (I - P_0)Tu_0) + O(h^2) \\ c) \quad \hat{v}_2 &= -(I - P_0)Tu_0 + O(h) \end{aligned} \tag{8.22}$$

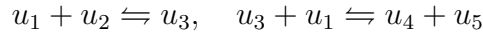
We take the limit $h \rightarrow 0$ to get

$$\begin{aligned} a) \quad \partial_t u &= PTu + \tilde{v} \\ b) \quad \partial_t \tilde{v} &= \dot{P}(\tilde{v} - (I - P)Tu), \quad \hat{v} = -(I - P)Tu \\ \tilde{v} &\in \tilde{S}(t), \quad \hat{v} \in \hat{S}(t). \end{aligned} \tag{8.23}$$

Which is a closed system for u, \tilde{v} which is the same as equation (5.14).

8.5 A Spatially Homogeneous Example

We again use the example first introduced in Section 2.4 where we have five species and two reactions as follows:



We used the same parameters as in section 6.3 which are listed in table 8.1. We compare the full and reduced AP schemes. For the full solution we solved equations (8.5), (8.6), and (8.7) and for the reduced solution we discretized equations (8.20) and (8.21) noting that $v_1 = \tilde{v}_1 + \hat{v}_1 = \tilde{v}_0 + \hat{v}_1$. This is used to discretize equation (8.20) as follows.

$$\begin{aligned} a) \quad u_1 &= (I - hT)^{-1}u_0 \\ b) \quad v_1 &= P_0v_0 - (I - P_0)Tu_1. \end{aligned} \tag{8.24}$$

Equation (8.21) is discretized as

$$\begin{aligned} a) \quad u_2 &= u_1 + hv_1 \\ b) \quad v_2 &= v_1 . \end{aligned} \tag{8.25}$$

Table 8.1: Parameters Used in Computing and Plotting Figure 8.1.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	0.5
Coefficient of the first backward reaction (α_1^b)	1
Coefficient of the second forward reaction (α_2^f)	0.5
Coefficient of the second backward reaction (α_2^b)	1
Separation of time scales (ϵ)	1×10^{-6}
Timestep (h)	0.01
Transport operator	$\text{diag}(-2, -1.5, -1, -0.5, 0)$

As you can see in Figure 8.1, the solutions match very well. We computed the norm of the difference of the full and reduced solutions over the norm of the full solution at the last time step. We got 1.7236×10^{-6} .

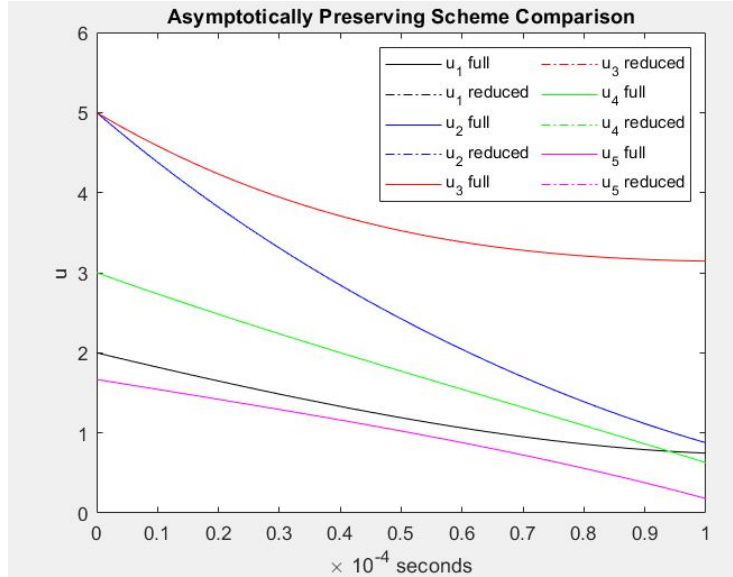
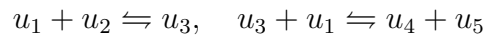


Figure 8.1: Comparison of Full to Reduced Solutions for the AP Scheme with Five Species and Two Reactions.

8.6 A Spatially Inhomogeneous Example

We again use the example first introduced in Section 2.4 where we have five species and two reactions as follows:



We used similar parameters as in section 6.4 which are listed in Table 8.2 for case 1 and Table 8.3 for case 2. We compare the full and reduced AP schemes. We used the same equations as in Section 8.5.

For the full solution we solved the scheme (6.3) for $t \in [0, 20] \times 10^{-4}$ and solved the reduced problem with the first order scheme explained in Section 6.1. In Figures 8.2 and 8.3, we show the results of the full and reduced solutions for cases one and two at $x = 0.25$ microns, $x = 0.55$ microns, and $x = 0.85$ microns. As you can see in

these figures, the solutions match very well. We computed the norm of the difference of the full and reduced solutions over the norm of the full solution at the last time step. We got 0.6083 for case one and 0.1504 for case two.

Table 8.2: Parameters Used in Computing and Plotting Figure 8.2.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	4
Coefficient of the first backward reaction (α_1^b)	0.1
Coefficient of the second forward reaction (α_2^f)	4
Coefficient of the second backward reaction (α_2^b)	0.1
Separation of time scales (ϵ)	1×10^{-6}
Timestep (h)	0.1
Spatial stepsize (Δx)	0.05
Diffusion Coefficient (D) ($-1 \times 10^{-4} \times$)	[1, 0.75, 0.5, 0.25, 0.0025]
Mobility (μ)	$diag(1, 1, 1, 1, 1)$
Electric Field ($\nabla_x V$)	2
Charge (z)	$diag(0, 0, 0, 0, 0)$

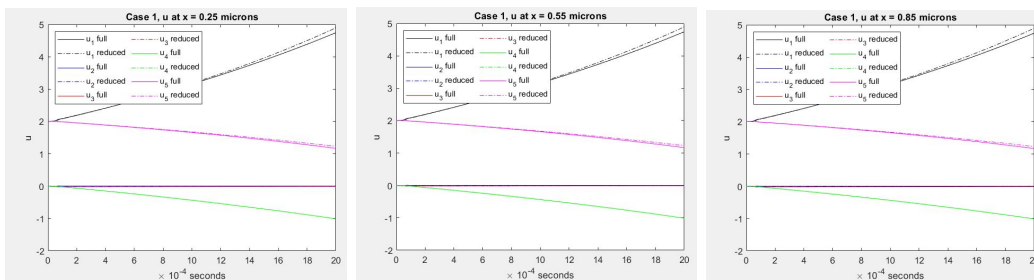


Figure 8.2: Case 1 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55$, and 0.85 Microns.

Table 8.3: Parameters Used in Computing and Plotting Figure 8.3.

Parameter	Value
Coefficient of the first forward reaction (α_1^f)	4
Coefficient of the first backward reaction (α_1^b)	0.1
Coefficient of the second forward reaction (α_2^f)	4
Coefficient of the second backward reaction (α_2^b)	0.1
Separation of time scales (ϵ)	1×10^{-2}
Timestep (h)	0.1
Spatial stepsize (Δx)	0.05
Diffusion Coefficient (D) ($-1 \times 10^{-4} \times$)	$[1, 0.75, 0.5, 0.25, 0.0025]$
Mobility (μ)	$diag(1, 1, 1, 1, 1)$
Electric Field ($\nabla_x V$)	2
Charge (z)	$diag(-1, 0, -1, 0, 0)$

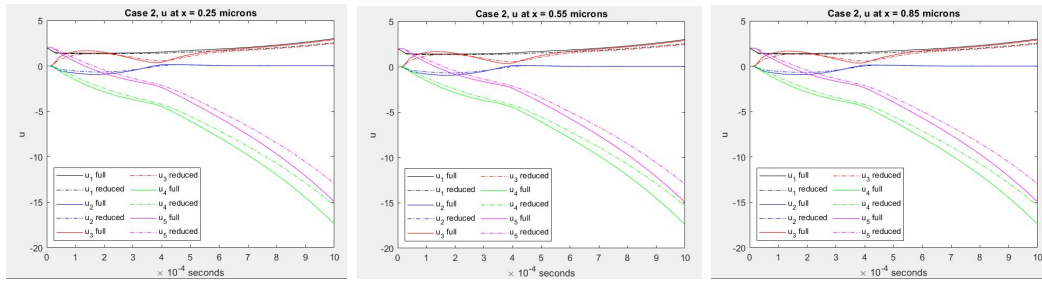


Figure 8.3: Case 2 Comparison of Full and Reduced Solutions at $x = 0.25, 0.55,$ and 0.85 Microns.

Chapter 9

EXAMPLE

Here we present a more realistic example applied to the simulation of degradation effects in solar cells.

9.1 Solar Cell

We begin with our list of items that degrade cadmium telluride which we introduced in Chapter 2. We use that list and derive the following list of 15 species.

1. e^- (electron)
2. Cu_i^- (copper interstitial)
3. Cu_i^0 (copper interstitial)
4. Cu_i^+ (copper interstitial)
5. Cu_{Cd}^- (copper cadmium)
6. Cu_{Cd}^0 (copper cadmium)
7. Cu_{Cd}^+ (copper cadmium)
8. Cu_{Cd}^{+2} (copper cadmium)
9. Cl_i^- (chlorine interstitial)
10. Cl_i^0 (chlorine interstitial)
11. Cl_i^+ (chlorine interstitial)

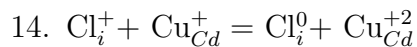
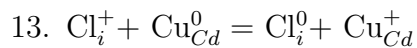
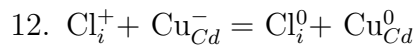
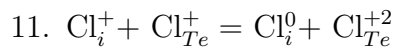
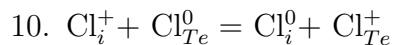
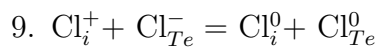
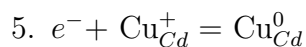
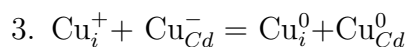
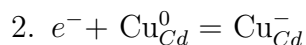
12. Cl_{Te}^- (chlorine telluride)

13. Cl_{Te}^0 (chlorine telluride)

14. Cl_{Te}^+ (chlorine telluride)

15. Cl_{Te}^{+2} (chlorine telluride)

Now we consider the following reactions:



We use a stoichiometry matrix to describe these 14 reactions involving the 15 species.

$$\begin{bmatrix} -1 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

The following three figures show how the species amounts change as we get deeper into the material. Figure 9.1 shows the species after only one time step. Figure 9.2 shows the species at $t = .5$ seconds and figure 9.3 shows the species at $t = 1$ second. Notice that as the time progresses the scales on each species plot change. This is a somewhat reduced model. There are no electron hole combinations. Only electrons. More work is needed to include electron hole combinations.

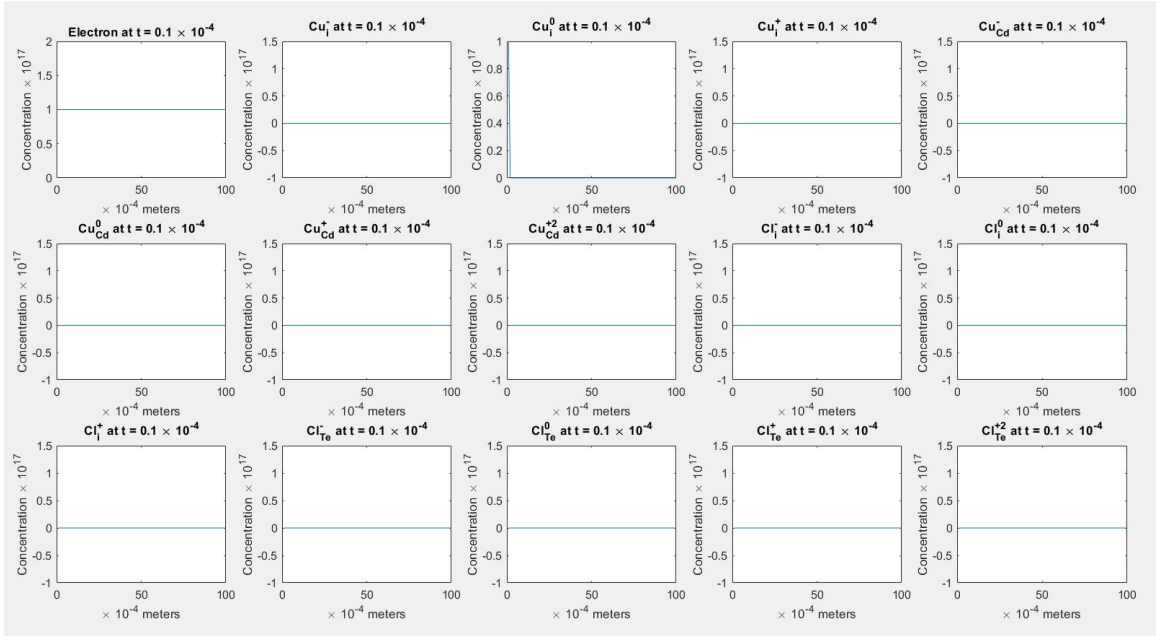


Figure 9.1: All of the Species at $t = 1 \times 10^{-5}$ Seconds, Which is After the First Time Step.

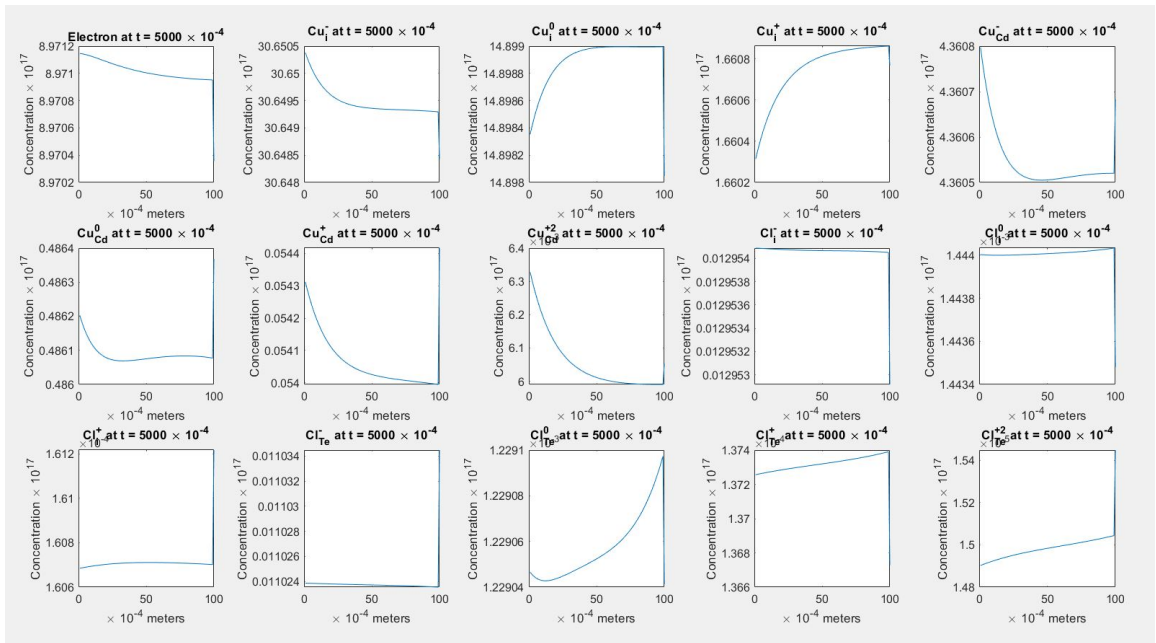


Figure 9.2: All of the Species at $t = 0.5$ Seconds.

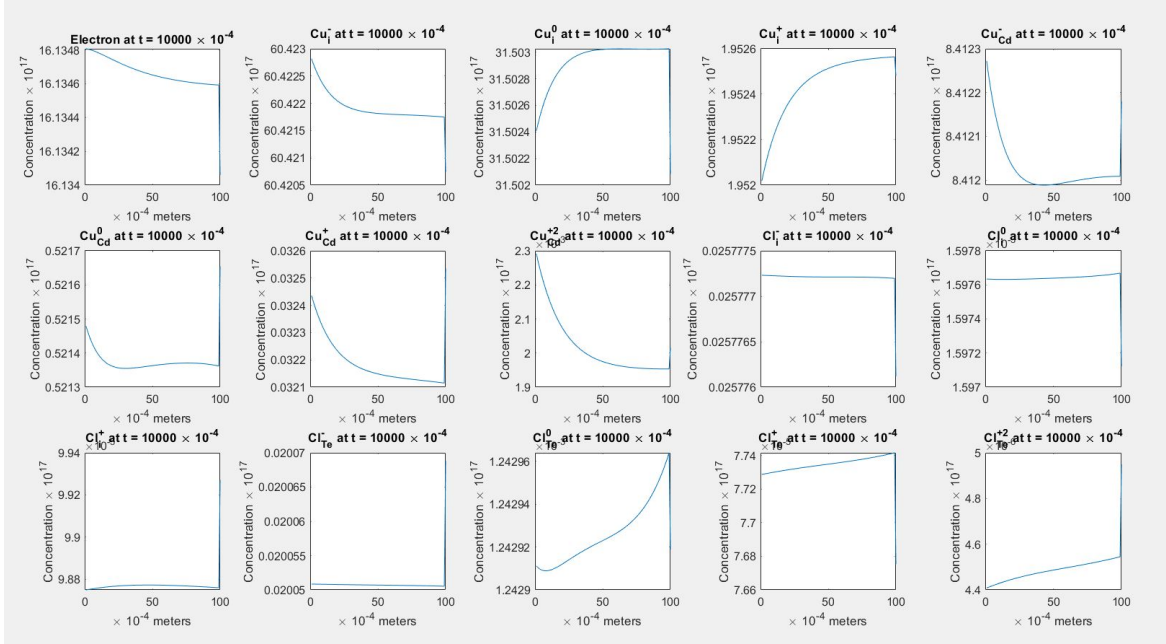


Figure 9.3: All of the Species at $t = 1$ Second.

Table 9.1 shows the parameters used in this model.

9.2 Conclusion

Throughout this work we have developed a methodology for general reaction transport problems on multiple time scales applicable to situations where we cannot explicitly compute quasi-steady state. For these general problems we have developed asymptotically preserving operator splitting methods which allow us to take large time steps using information about the asymptotic solutions. We applied this solution to the specific problem of solar cells but there could be other applications. Future work in this area will improve the physics of the example in Section 9.1 and explore applications to biological and other problems.

Table 9.1: Parameters Used in Computing and Plotting Figures 9.1, 9.2, and 9.3.

Parameter	Value														
Separation of time scales (ϵ)	1×10^{-7}														
Timestep (h)	1×10^{-5} seconds														
Spatial stepsize (Δx)	0.01 microns														
Electric Field ($\nabla_x V$)	2 eV														

Species	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
μ	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
D	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
z	-1	-1	0	1	-1	0	1	2	-1	0	1	-1	0	1	2

REFERENCES

- Albin, D. S., *Correlations of capacitance-voltage hysteresis with thin-film CdTe solar cell performance during accelerated lifetime testing*, Conference paper (National Renewable Energy Laboratory (U.S.)) ; NREL/CP-5200-47761 (National Renewable Energy Laboratory, Golden, CO], 2011).
- Ascher, U. M., S. J. Ruuth and R. J. Spiteri, “Implicit-explicit Runge-Kutta methods for time-dependent partial differential equations”, *Applied Numerical Mathematics* **25**, 2-3, 151–167 (1997).
- Bisi, M., F. Conforto and L. Desvillettes, “QUASISTEADYSTATE APPROXIMATION FOR REACTIONDIFFUSION EQUATIONS”, *Bulletin of the Institute of Mathematics, Academia Sinica* **2**, No. 4, 823–850 (2007).
- Bogacki, P., “Linear Algebra Toolkit”, <http://www.math.odu.edu/~bogacki/cgi-bin/lat.cgi> (2019).
- Boltzmann, L., *Lectures on gas theory* (Dover Publications, New York, 1995), dover edn.
- Brown, T. L., ed., *Chemistry: the central science* (Pearson Prentice Hall, Upper Saddle River, NJ, 2008), 11th edn.
- Brush, S. G., *The Chapman-Enskog solution of the transport equation for moderately dense gases*, no. S. G. Brush ; Vol. 3 in *Kinetic theory* (Pergamon Press, Oxford, 1972), oCLC: 31990387.
- Caffisch, R. E., S. Jin and G. Russo, “Uniformly Accurate Schemes for Hyperbolic Systems with Relaxation”, *SIAM Journal on Numerical Analysis* **34**, 1, 246–281 (1997).
- Dimarco, G. and L. Pareschi, “Exponential RungeKutta Methods for Stiff Kinetic Equations”, *SIAM Journal on Numerical Analysis* **49**, 5, 2057–2077 (2011).
- Enskog, D., “Bemerkungen zu einer Fundamentalgleichung in der kinetischen Gas-theorie (Remarks on a fundamental equation in kinetic gas theory)”, *Physik Zeits* **12**, 533 (1911a).
- Enskog, D., “Über eine Verallgemeinerung der zweiten Maxwellschen Theorie der Gase (On a generalization of the second Maxwell theory of gases)”, *Physik Zeits* **12**, 56 (1911b).
- Erdi, P. and J. Toth, *Mathematical models of chemical reactions: theory and applications of deterministic and stochastic models*, *Nonlinear science: theory and applications* (Manchester Univ. Pr, Manchester, 1989), oCLC: 246618543.

- Flowers, P., K. Theopold, R. Langley, W. R. Robinson, M. Blaser, S. Bott, D. Carpenetti, A. Eklund, E. El-Giar, D. Frantz, P. Hooker, G. Kaminski, J. Look, C. Martinez, T. Milliken, V. Moravec, J. D. Powell, T. Sorensen, A. Soult and OpenStax College, *Chemistry* (OpenStax College Rice University 6100 Main Street MS-375 Houston, Texas 77005, 2018), oCLC: 1061188298.
- Higham, D. J., “An Algorithmic Introduction to Numerical Simulation of Stochastic Differential Equations”, *SIAM Review* **43**, 3, 525–546 (2001).
- Holmes, M. H., *Introduction to Perturbation Methods*, no. 20 in Texts in applied mathematics (Springer, New York, 2013), 2nd ed edn., oCLC: ocn839305658.
- Honsberg, C. and S. Bowden, “PVCDROM”, pveducation.org (2019).
- Jordan, D. C. and S. R. Kurtz, “Photovoltaic Degradation Rates - An Analytical Review”, *Progress in Photovoltaics: Research and Applications* (2012).
- LeVeque, R. J., *Finite difference methods for ordinary and partial differential equations: steady-state and time-dependent problems* (Society for Industrial and Applied Mathematics, Philadelphia, PA, 2007), oCLC: ocm86110147.
- Macaulay, D., *The way things work* (Houghton Mifflin, Boston, 1988).
- MacNamara, S. and G. Strang, “Chapter 3. Operator Splitting”, in “Splitting Methods in Communication and Imaging, Science, and Engineering”, (Springer international Publishing, Switzerland, 2016).
- Maxwell, L., “III. On stresses in rarefied gases arising from inequalities of temperature”, *Proceedings of the Royal Society of London* **27**, 185-189, 304–308 (1878).
- Morita, K., H. Kato, I. Tsuda and Y. Hishikawa, “Degradation factor analysis of crystalline-Si PV modules through long-term field exposure test”, *Proceedings of the 3rd Conference on Photovoltaic Energy Conversion, Osaka, Japan* (2003).
- Neamen, D. A., *Semiconductor physics and devices: basic principles* (McGraw-Hill, New York, NY, 2012), 4th ed edn., oCLC: ocn681739179.
- Neiburger, M., J. G. Edinger and W. D. Bonner, *Understanding our atmospheric environment* (W.H. Freeman, San Francisco, 1982), 2nd ed edn.
- Osterwald, C. R., A. Anderberg, S. Rummel and L. Ottoson, “Degradation analysis of weathered crystalline-silicon PV modules”, in “Conference Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conference, 2002.”, pp. 1392–1395 (2002).
- Pierret, R. F., *Semiconductor device fundamentals* (Addison-Wesley, Reading, Mass, 1996).
- Ringhofer, C., “ASYMPTOTICALLY PRESERVING NUMERICAL METHODS FOR LARGE REACTION DIFFUSION SYSTEMS WITH APPLICATIONS TO SOLAR CELL DESIGN”, (2018).

- Rosenbom, E. J., “The Mathematical Theory of Non-Uniform Gases (Chapman, S.; Cowling, T. G.)”, *Journal of Chemical Education* **18**, 1, 48 (1941).
- Selberherr, S., *Analysis and simulation of semiconductor devices* (Springer-Verl, Wien, 1984), oCLC: 251592380.
- Sportisse, B., “An Analysis of Operator Splitting Techniques in the Stiff Case”, *Journal of Computational Physics* **161**, 1, 140–168 (2000).
- Strang, G., “The fundamental theorem of linear algebra”, *The American Mathematical Monthly* **100**, 9, 848–855 (1993).
- Strang, G., *Introduction to linear algebra* (Wellesley-Cambridge Press, Wellesley, Mass, 2009), 4. ed edn., oCLC: 298178914.
- TamizhMani, G. and J. Kuitche, “Accelerated Lifetime Testing of Photovoltaic Modules”, (2013).
- van Roosbroeck, W., “Theory of flow of electrons and holes in germanium and other semiconductors”, *Bell System Technical Journal* **29**, 560–607 (1950).
- Vook, D., M. Cao, P. Vande Voorde, R. Dutton, Z. Yu and M. Ancona, “Density-gradient analysis of MOS tunneling”, *IEEE Transactions on Electron Devices* **47**, 12, 2310–2319 (2000).
- Wohlgemuth, J., “Reliability testing of PV modules”, in “Proceedings of 1994 IEEE 1st World Conference on Photovoltaic Energy Conversion - WCPEC (A Joint Conference of PVSC, PVSEC and PSEC)”, vol. 1, pp. 889–892 (IEEE, Waikoloa, HI, USA, 1994).
- Wohlgemuth, J. H., “Assessing the Trends in Module Field Failures”, in “2018 IEEE 7th World Conference on Photovoltaic Energy Conversion (WCPEC) (A Joint Conference of 45th IEEE PVSC, 28th PVSEC & 34th EU PVSEC)”, pp. 0092–0097 (IEEE, Waikoloa Village, HI, 2018).

APPENDIX A
A SIMPLE EXAMPLE

The following is a simple example of the discussion presented in section 5.3. We begin with one reaction and three species. Let the species be u_1, u_2 , and u_3 with the reaction $u_1 + u_2 \rightarrow u_3$. In this example we have the following

$$\begin{aligned}\dot{u}_1 &= -u_1u_2 \\ \dot{u}_2 &= -u_1u_2 \\ \dot{u}_3 &= u_1u_2\end{aligned}$$

The stoichiometry matrix is $S = (-1 \ -1 \ 1)$. As stated above in Section 5.1, C is the basis of the null space of S which we compute following (Bogacki (2019)). We transform S to the reduced row echilon form to get $(1 \ 1 \ -1)$. This corresponds to the system $x_1 + x_2 - x_3 = 0$. This system has infinitely many solutions

$$x_1 = -x_2 + x_3, \quad x_2 = \text{arbitrary}, \quad x_3 = \text{arbitrary}$$

We select $x_2 = -1$ and $x_3 = 0$. This gives us $(1 \ -1 \ 0)^T$. Next we select $x_2 = 0$ and $x_3 = 1$. This gives us $(1 \ 0 \ 1)^T$ which gives us

$$r = \begin{bmatrix} -u_1u_2 \\ -u_1u_2 \\ u_1u_2 \end{bmatrix}, \quad R = \begin{bmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{bmatrix} \quad C = \begin{bmatrix} 1 & 1 \\ -1 & 0 \\ 0 & 1 \end{bmatrix} \quad G = \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ 0 & 1 \end{bmatrix}.$$

We also see that $C^T R = 0$ and so we choose $P = G(C^T G)^{-1} C^T$. Let us check these with our example

$$C^T \cdot R = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{bmatrix} = \begin{bmatrix} -u_2 + u_2 & -u_1 + u_1 & 0 \\ -u_2 + u_2 & -u_1 + u_1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\text{and} \quad R \cdot G = \begin{bmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{bmatrix} \cdot \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} -u_2u_1 + u_1u_2 & 0 \\ -u_2u_1 + u_1u_2 & 0 \\ u_2u_1 - u_1u_2 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}.$$

Now we compute $P = G(C^T G)^{-1} C^T$ in our example. We begin with the middle,

$$(C^T G) = \begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} u_1 + u_2 & 0 \\ u_1 & 1 \end{bmatrix}.$$

Now we use Cramer's Rule (Strang (2009)) to find the inverse.

$$(C^T G)^{-1} = \frac{1}{u_1 + u_2} \begin{bmatrix} 1 & 0 \\ -u_1 & u_1 + u_2 \end{bmatrix}.$$

Now we multiply by the first term on the left

$$G(C^T G)^{-1} = \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ -u_1 & u_1 + u_2 \end{bmatrix} = \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ -u_1 & u_1 + u_2 \end{bmatrix}.$$

And now multiply by the last term on the right will give us P

$$\begin{aligned} P &= G(C^T G)^{-1} C^T = \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & 0 \\ -u_2 & 0 \\ -u_1 & u_1 + u_2 \end{bmatrix} \cdot \begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \\ &= \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix}. \end{aligned}$$

Now we check that $PR = RP = 0$.

$$\begin{aligned} PR &= \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \cdot \begin{bmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{bmatrix} \\ &= \frac{1}{u_1 + u_2} \begin{bmatrix} -u_1 u_2 + u_1 u_2 & -u_1^2 + u_1^2 & 0 \\ u_2^2 - u_2^2 & u_2 u_1 - u_2 u_1 & 0 \\ -u_2^2 - u_1 u_2 + u_1 u_2 + u_2^2 & -u_2 u_1 - u_1^2 + u_1^2 + u_2 u_1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \end{aligned}$$

$$\begin{aligned} RP &= \frac{1}{u_1 + u_2} \begin{bmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{bmatrix} \cdot \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \\ &= \frac{1}{u_1 + u_2} \begin{bmatrix} -u_2 u_1 + u_1 u_2 & u_2 u_1 - u_1 u_2 & 0 \\ -u_2 u_1 + u_1 u_2 & u_2 u_1 - u_1 u_2 & 0 \\ u_2 u_1 - u_1 u_2 & -u_2 u_1 + u_1 u_2 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \end{aligned}$$

Now we check that $P^2 = P$

$$\begin{aligned} P^2 &= \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \cdot \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \\ &= \frac{1}{(u_1 + u_2)^2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \cdot \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} \\ &= \frac{1}{(u_1 + u_2)^2} \begin{bmatrix} u_1^2 + u_1 u_2 & -u_1^2 - u_1 u_2 & 0 \\ -u_2 u_1 - u_2^2 & u_2 u_1 + u_2^2 & 0 \\ u_2 u_1 - u_1 u_2 + (u_1 + u_2) u_2 & -u_2 u_1 + u_1 u_2 + (u_1 + u_2) u_1 & (u_1 + u_2)^2 \end{bmatrix} \end{aligned}$$

$$\begin{aligned} &= \frac{1}{(u_1 + u_2)^2} \begin{bmatrix} u_1(u_1 + u_2) & -u_1(u_1 + u_2) & 0 \\ -u_2(u_1 + u_2) & u_2(u_1 + u_2) & 0 \\ u_2(u_1 + u_2) & u_1(u_1 + u_2) & (u_1 + u_2)^2 \end{bmatrix} \\ &= \frac{1}{u_1 + u_2} \begin{bmatrix} u_1 & -u_1 & 0 \\ -u_2 & u_2 & 0 \\ u_2 & u_1 & u_1 + u_2 \end{bmatrix} = P. \end{aligned}$$

APPENDIX B
GUMMEL'S METHOD

This is essentially the same as the presentation in section 7.2 however, here we treat the one species case before we discuss N species case. Gummel's method is an iterative method which shifts the nonlinearity from the transport equations to the Poisson equation using a variable transformation. Given N species, we have the following Poisson drift diffusion problem

$$\partial_t^2 V = \sum_n z_n u_n + d$$

$$\partial_t u_n = \partial_x (D_n \partial_x u_n + z_n \mu_n u_n \partial_x V), \quad n = 1 : N \quad (\text{B.1})$$

We start by treating one species plus Poisson. We begin with one species and a model equation of the form

$$\partial_t u = \partial_x [A(\partial_x u + u \partial_x \psi)], \quad \partial_x^2 \psi = -u + d.$$

We introduce a variable transformation. We set $\rho = e^\psi u$ which gives us

$$\partial_t (e^{-\psi} \rho) = \partial_x (A e^{-\psi} \partial_x \rho), \quad \partial_x^2 \psi = -e^{-\psi} \rho + d.$$

Now we apply the method of lines discretization (LeVeque (2007)) to get

$$\partial_t (e^{-\psi_j} \rho_j) = \frac{f_{j+0.5} - f_{j-0.5}}{\Delta x}, \quad f_{j+0.5} = \frac{A}{\Delta x} e^{-\psi_{j+0.5}} (\rho_{j+1} - \rho_j) \quad (\text{B.2})$$

$$\frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{\Delta x^2} = e^{-\psi_j} \rho_j + d_j. \quad (\text{B.3})$$

We apply the Gummel iteration with index k to get

$$\frac{\psi_{j+1}^k - 2\psi_j^k + \psi_{j-1}^k}{\Delta x^2} = e^{-\psi_j^k} \rho_j^{k-1} + d_j$$

and this gives us ψ_j^k for all j . We apply this to equation (B.2) to get

$$e^{-\psi_j} \rho_j |^k = e^{-\psi_j} \rho_j(t) + \Delta t \left(\frac{f_{j+0.5} - f_{j-0.5}}{\Delta x} \right), \quad f_{j+0.5} = \frac{A}{\Delta x} e^{-\psi_{j+0.5}} (\rho_{j+1} - \rho_j) |_{t+\Delta t}^{k+1}$$

Now we present a preliminary algorithm for one time step. We set $\rho_j^0 = \rho_j(t)$ and $\psi_j^0 = \psi_j(t)$. Then we solve

$$\frac{\psi_{j+1}^k - 2\psi_j^k + \psi_{j-1}^k}{\Delta x^2} = e^{-\psi_j^k} \rho_j^{k-1} + d_j, \quad k = 1 : K$$

And this will give us ψ_j^k for $k = 1 : K$ and for all j . Note that this is still a nonlinear equation in ψ so it still has to be solved by a Newton type method.

Next we solve

$$e^{-\psi_j^k} \rho_j^k = e^{-\psi_j} \rho_j(t) + \Delta t \left(\frac{f_{j+0.5} - f_{j-0.5}}{\Delta x} \right), \quad (\text{B.4})$$

$$f_{j+0.5} = \frac{A}{\Delta x} e^{-\psi_{j+0.5}} (\rho_{j+1} - \rho_j)^k, \quad k = 1 : K \quad (\text{B.5})$$

And this will give us ρ_j^k for $k = 1 : K$ and for all j . Since we already know the $\psi_{j+0.5}^k$ this is linear for ρ_j^k , therefore we have shifted the nonlinearity from the transport equation to the Poisson equation.

Now we set $\psi_j(t + \Delta t) = \psi_j^K$ and $\rho_j(t + \Delta t) = \rho_j^K$.

Note that we compute $\psi_{j+0.5}$ by interpolating between ψ_j and ψ_{j+1} . In this way we set

$$\exp(-\psi_{j+0.5}) = \exp\left(-\frac{1}{2}(\psi_j + \psi_{j+1})\right).$$

Using this we have that

$$f_{j+0.5} = \frac{A}{\Delta x} \exp\left(-\frac{1}{2}(\psi_j + \psi_{j+1})\right) (\rho_{j+1} - \rho_j).$$

We recall that $\rho = e^\psi u$ and eliminate ρ to get

$$f_{j+0.5} = \frac{A}{\Delta x} \left[\exp\left(\frac{\psi_{j+1} - \psi_j}{2}\right) u_{j+1} - \exp\left(\frac{\psi_j - \psi_{j+1}}{2}\right) u_j \right].$$

Using this we present a final algorithm for one time step.

We set $u_j^0 = u_j(t)$ and $\psi_j^0 = \psi_j(t)$. Then we solve

$$\frac{\psi_{j+1}^k - 2\psi_j^k + \psi_{j-1}^k}{\Delta x^2} = [\exp(\psi_j^{k-1} - \psi_j^k)] u_j^{k-1} + d_j, \quad k = 1 : K$$

And this will give us ψ_j^k for $k = 1 : K$ and for all j .

Next we solve

$$\begin{aligned} u_j^k &= u_j(t) + \Delta t \left(\frac{f_{j+0.5} - f_{j-0.5}}{\Delta x} \right), \\ f_{j+0.5} &= \frac{A}{\Delta x} \left[\exp\left(\frac{\psi_{j+1} - \psi_j}{2}\right) u_{j+1} - \exp\left(\frac{\psi_j - \psi_{j+1}}{2}\right) u_j \right] \Bigg|^k, \quad k = 1 : K \end{aligned} \quad (\text{B.6})$$

And this will give us u_j^k for $k = 1 : K$ and for all j .

Now we set $\psi_j(t + \Delta t) = \psi_j^K$ and $u_j(t + \Delta t) = u_j^K$.

Now we expand the one species algorithm to an N species algorithm. We begin with equation (B.1) and use the Einstein relations, U_T is the ambient thermal energy ($U_T \approx 0.025eV$ at 300 kelvin). We also set $U_T = D_n/\mu_n$ for all n and get

$$\partial_t u_n = \partial_x (D_n \partial_x u_n + z_n \mu_n u_n \partial_x V) = \partial_x [D_n (\partial_x u_n + \frac{z_n}{U_T} u_n \partial_x V)], \quad n = 1 : N$$

Now we set $A = D_n$ and $\psi = \frac{z_n}{U_T} V$. This gives us an algorithm for one time step in V, u_1, \dots, u_N .

We set $u_{n,j}^0 = u_{n,j}(t)$ and $V_j^0 = V_j(t)$. Then we solve

$$\frac{V_{j+1}^k - 2V_j^k + V_{j-1}^k}{\Delta x^2} = \sum_n \exp \left[\frac{z_n}{U_T} (V_j^{k-1} - V_j^k) \right] z_n u_{n,j}^{k-1} + d_j, \quad k = 1 : K$$

And this will give us ψ_j^k for $k = 1 : K$ and for all n and j .

Next we solve

$$u_{n,j}^k = u_{n,j}(t) + \Delta t \left(\frac{f_{j+0.5} - f_{j-0.5}}{\Delta x} \right),$$

$$f_{j+0.5} = \frac{A}{\Delta x} \left[\exp(z_n \frac{V_{j+1} - V_j}{2U_T}) u_{n,j+1} - \exp(z_n \frac{V_j - V_{j+1}}{2U_T}) u_{n,j} \right] \Bigg|^k, \quad k = 1 : K \quad (\text{B.7})$$

And this will give us $u_{n,j}^k$ for $k = 1 : K$ and for all n and j .

Now we set $V_j(t + \Delta t) = V_j^K$ and $u_{n,j}(t + \Delta t) = u_{n,j}^K$.