

# Battery Computing

An MMSC Case Study on **SCIENTIFIC COMPUTING**

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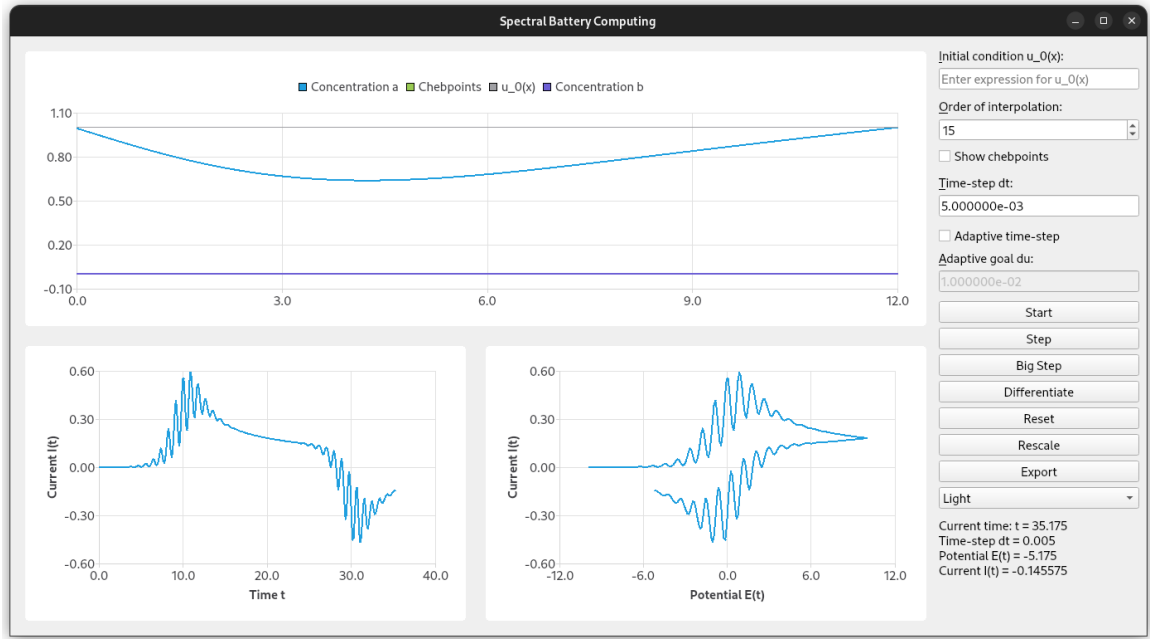
## Abstract

This work shall attempt to

**Our Goal:** Numerically obtain the solution  $\{a(x, T), b(x, T)\}$  of

$$\begin{cases} \frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2}, & a : \mathbb{R}^+ \times [0, T] \mapsto [0, 1], T \in \mathbb{R}^+, D_a \in \mathbb{R}^+, \\ \frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2}, & b : \mathbb{R}^+ \times [0, T] \mapsto [0, 1], D_b \in \mathbb{R}^+, \\ a(\infty, t) = 1, b(\infty, t) = 0 & \forall t \in [0, T] \\ a(x, 0) = 1, b(x, 0) = 0 & \forall x \in (0, \infty) \\ a(0, t) = 0, \frac{\partial a}{\partial x} + D \frac{\partial b}{\partial x} = 0 \end{cases}$$

The implementation bla bla



**Figure 1:** Graphical User Interface

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# 1 Problem Introduction

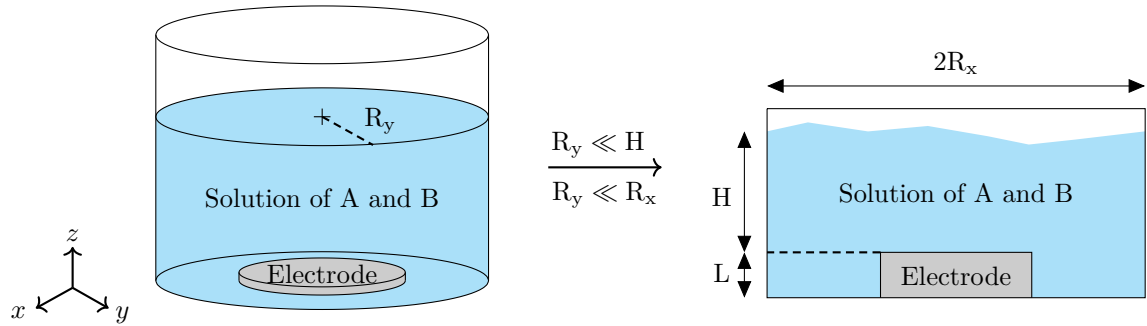
Energy storage and its associated challenges are clearly among the most relevant questions, not only for the industrial but also the private sector. Politically, many nations in the world are steering towards greener energy supplies. Renewable energy sources such as wind and sun usually have a fundamental issue however, their availability is subject to an immense amount of fluctuation, which the energy grid must compensate through short- and long-term energy storage.

Long-term solutions include for example pumped-storage hydroelectricity facilities, but these must be complemented with short-term storage approaches such as Lithium-Ion or Lithium-Iron-Phosphate ( $\text{LiFePO}_4$ ) batteries. Most modern batteries exploit electrochemical reactions to relate electrical potentials with chemical potentials and their associated difference ( $\rightarrow$  voltage). The oxidation reaction we considere here is



where  $A$  and  $B$  can be any chemicals and  $e^-$  is an electron (Gavaghan and Bond 2000).

More bla bla later on.



**Figure 2:** Wohoo.

As stated on Page 1, we consider the following Partial Differential Equation (PDE)s in the concentrations  $a, b \in \mathbb{C}^2(\Omega)$

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} \quad (1)$$

$$\frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2} \quad (2)$$

## 1.1 Chronoamperometry

## 1.2 Linear Sweep Voltammetry

## 1.3 Linear Sweep AC Voltammetry

# 2 Mathematical Background

Let  $\mathbb{N}$  denote the nonnegative integers, so  $0 \in \mathbb{N}$ . Similarly, let  $\mathbb{R}^+ = [0, \infty)$  denote the nonnegative real numbers.

## 2.1 Laplace Integral Transform

What is Laplace?

### 2.1 Definition: Laplace Integral Transform

Given a function  $a : \mathbb{R} \mapsto \mathbb{R}$ , its Laplace transform  $\hat{a} : \mathbb{C} \mapsto \mathbb{C}$  is given by

$$\hat{a}(s) = \mathcal{L}\{a\}(s) = \int_0^\infty a(t)e^{-st} dt.$$

Laplace transforms are especially valuable for physical systems as many of them expose exponentially decaying and/or periodic behaviours which the Laplace transform is well-suited for due to the form of its kernel. Decaying behaviour is captured by the real component of the argument  $s$ ,  $\Re(s)$ , whereas periodicities are captured by the imaginary part  $\Im(s)$ <sup>1</sup>.

### 2.1 Theorem: Laplace Transform of the Derivative

Given a function  $a(t)$  and a corresponding Laplace-transform  $\hat{a}(s) = \mathcal{L}\{a\}(s)$ , the transform of the derivative  $a'(t)$  of the original function is given by

$$\mathcal{L}\{a'\}(s) = \mathcal{L}\left\{t \mapsto \frac{\partial a}{\partial t}\right\}(s) = s\hat{a}(s) - a_0,$$

where  $a_0 := a(t=0)$ .

<sup>1</sup>Consider for comparison the Fourier transform  $\mathcal{F}(a)(\omega) := \int_{-\infty}^\infty a(t)e^{i\omega t} dt$  which captures periodic frequencies, where the kernel automatically follows multiplication along the unit circle due to the imaginary-valued exponent  $i\omega t$  (the argument  $\omega \in \mathbb{R}$  is real-valued). Intuitively, the Laplace transform coincides with the Fourier transform if evaluated at  $s = i\omega$ .

*Proof.* Proof for Laplace's differentiation theorem. □

### 2.2 Theorem: Initial Value

For a function  $a \in \mathcal{C}^2(\Omega)$  with corresponding Laplace-transform  $\hat{a} = \mathcal{L}\{a\}$ ,

$$\lim_{s \rightarrow \infty} s\hat{a}(s) = \lim_{t \rightarrow 0^+} a(t)$$

relates  $a$ 's *initial value* with the transform evaluated at  $s \rightarrow \infty$ .

### 2.3 Theorem: Laplace Convolution

For a function  $a \in \mathcal{C}^2(\Omega)$  with corresponding Laplace-transform  $\hat{a} = \mathcal{L}\{a\}$ ,

$$\lim_{s \rightarrow \infty} s\hat{a}(s) = \lim_{t \rightarrow 0^+} a(t)$$

relates  $a$ 's *initial value* with the transform evaluated at  $s \rightarrow \infty$ .

## 2.2 Chebyshev Polynomials

### 2.2 Definition: Chebyshev polynomial

Chebyshev<sup>2</sup> polynomials  $T_k : \mathbb{R} \mapsto \mathbb{R}$  are functions satisfying

$$T_k(x) = T_k(\cos \theta) := \cos(k\theta) = \frac{1}{2}(z^k + z^{-k})$$

$$z := e^{i\theta}, \quad x := \Re(z) = \cos(\theta) = \frac{1}{2}(z + z^{-1})$$

for degree  $k \in \mathbb{N}$ . Then,  $T_0(x) = 1$ ,  $T_1(x) = x$ ,  $T_2(x) = 2x^2 - 1$ , and so on.

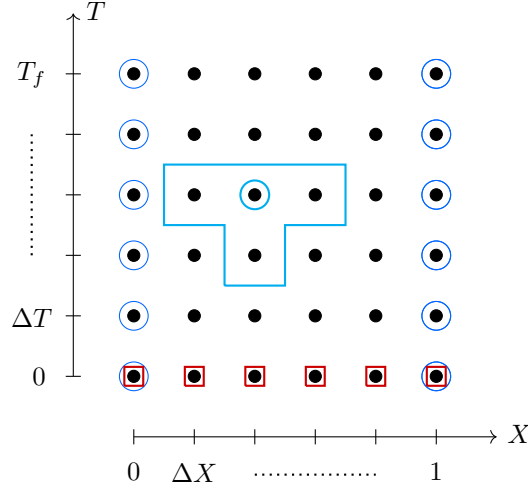
Proof of  $U_k(-1)$ 's value.

## 3 Finite Differences

Construct  $A\mathbf{x} = \mathbf{b}$ .

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<sup>2</sup>Named after Pafnuty Lvovich Chebyshev, alternatively transliterated as Tchebycheff, Tchebyshev (French) or TSCHEBYSCHOW (German).



**Figure 3:** Schematic of the finite different scheme where ... are the nodes specified by initial conditions, and ... are the nodes specified by boundary conditions.

### 3.1 Results

## 4 Analytical Approaches

When  $D = 1$ ,  $a + b = 1$  because.

### 4.1 Similarity Solution

### 4.2 Voltammetry Integral Equation

#### 4.2.1 Derivation using the Laplace Transform

As mentioned above, the Laplace Integral Transform is especially useful in the context of differential equations, mostly due to Theorem 2.1. Applying it to our *partial* differential diffusion equation Equation (1) transforms the problem into one of solving an *ordinary* differential equation. Similarly, ODEs could be turned into algebraic equations using a similar approach.

Starting from Equation (1), we Laplace-transform both sides and then apply Theorem 2.1 in time  $t$  to arrive at

$$\begin{aligned} \frac{\partial a}{\partial t} &= D_a \frac{\partial^2 a}{\partial x^2} && \text{Laplace-transform w.r.t. } t \\ \mathcal{L} \left\{ t \mapsto \frac{\partial a}{\partial t} \right\} &= D_a \mathcal{L} \left\{ t \mapsto \frac{\partial^2 a}{\partial x^2} \right\} && \text{Use Theorem 2.1} \\ s\hat{a}(s) - a_0(x) &= D_a \frac{\partial^2 \hat{a}}{\partial x^2} && \text{Rearrange} \\ \frac{\partial^2 \hat{a}}{\partial x^2} - \frac{s}{D_a} \hat{a} &= -\frac{a_0(x)}{D_a} \end{aligned}$$

where  $\hat{a} := \mathcal{L}\{a\}$  and  $a_0(x) := a(x, t = 0)$ , which is a second-order constant-coefficient Ordinary Differential Equation in space  $x$ . Its characteristic polynomial is  $\lambda^2 + \frac{s}{D_a} = 0$  which, together with the initial condition  $a_0 = 1$  and resulting particular solution  $\hat{a}_p(s, x) = \mathcal{L}\{-1\}(s) = \frac{1}{s^3}$ , leads us to the homogeneous solution

$$\hat{a}(s, x) = c_1 e^{\sqrt{\frac{s}{D_a}} x} + c_2 e^{-\sqrt{\frac{s}{D_a}} x} + \frac{1}{s}, \quad c_1, c_2 \in \mathbb{R}. \quad (3)$$

The constant  $c_1$  then vanishes when applying the initial value theorem (Theorem 2.2)

$$\lim_{s \rightarrow \infty} s\hat{a}(s) = \lim_{s \rightarrow \infty} \underbrace{c_1 s e^{\sqrt{\frac{s}{D_a}} x}}_{\rightarrow \infty} + \underbrace{c_2 s e^{-\sqrt{\frac{s}{D_a}} x}}_{\rightarrow 0} + 1 = \lim_{t \rightarrow 0^+} a(t) = 1$$

because  $c_1 \neq 0$  would cause its corresponding term to explode. Considering the other boundary condition

$$\left. \frac{\partial a}{\partial x} \right|_{x=0} = I(t) \quad \Leftrightarrow \quad \frac{\partial \hat{a}}{\partial x} = \hat{I}(s) := \mathcal{L}\{I\}(s)$$

, we obtain  $c_2 = \frac{-\hat{I}}{\sqrt{s}}$ . So Equation (3) becomes

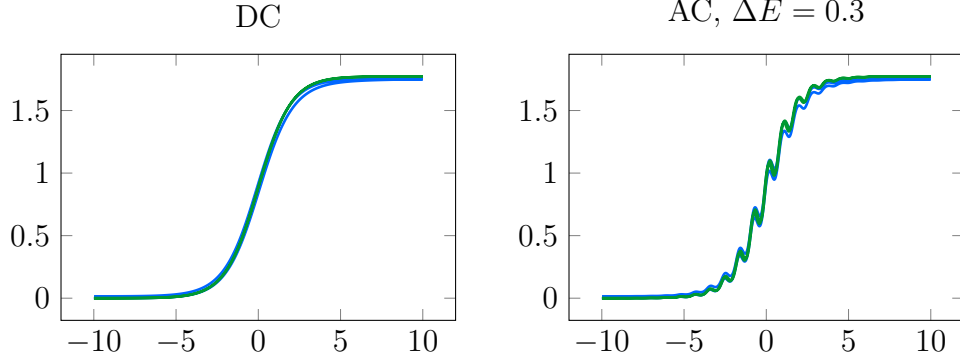
$$\hat{a}(s, x) = c_2 e^{-\sqrt{\frac{s}{D_a}} x} + \frac{1}{s}, \quad c_2 \in \mathbb{R}, \quad (4)$$

which, evaluated at  $x = 0$ , becomes  $\hat{a}(s, 0) = c_2 + \frac{1}{s}$ .

---


$$^3 \mathcal{L}\{1\} = \int_0^\infty e^{-st} dt = \frac{1}{s} [e^{-st}]_0^\infty = \frac{-1}{s}.$$

### 4.2.2 Numerical Solution



**Figure 4:** Convolution Integrals

## 5 Spectral Method

From the definition of Chebyshev polynomials  $T_k(x) = \cos(k\theta)$  (Definition 2.2), we can derive that

$$\frac{dT_k}{dx} = \frac{dT_k}{d\theta} \frac{d\theta}{dx} = \dots = kU_{k-1}(x),$$

where  $U_k : [-1, 1] \mapsto \mathbb{R}$  denote the Chebyshev polynomials of the second kind, which in turn are defined by

$$U_k(\cos \theta) \sin(\theta) = \sin((n+1)\theta).$$

In order to enforce a von-Neumann boundary condition on the left and a Dirichlet boundary condition on the right, we are interested in explicitly setting coefficients  $a_k$  such that

$$a_x(-1, t) = \left. \frac{da}{dx} \right|_{x=-1} = \tilde{l} \quad \text{and} \quad a(1) = r, \quad \text{where} \quad \tilde{l}, r \in \mathbb{R}.$$

Using the Chebyshev series ansatz

$$a(x, t) = \sum_{k=0}^{N-1} a_k^{(t)} T_k(x)$$

we have that

$$\frac{da}{dx} = \sum_{k=0}^{N-1} a_k^{(t)} \frac{dT_k}{dx}(x),$$

so we are interested in

$$a_x(-1, t) = \left. \frac{da}{dx} \right|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} \left. \frac{dT_k}{dx} \right|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} kU_{k-1}(-1).$$



Following from TODO (explained on Wikipedia), we know that

$$U_k(-1) = (-1)^k(k+1) \quad \text{and} \quad T_k(1) = 1 \quad \forall k \in \mathbb{N},$$

which turns our conditions into algebraic conditions w.r.t. the coefficients  $a_k^{(t)}$ ,

$$a_x(-1, t) = \left. \frac{da}{dx} \right|_{x=-1} = \sum_{k=0}^{N-1} a_k^{(t)} k^2 (-1)^{k-1} \stackrel{!}{=} \tilde{l} \quad \text{and} \quad a|_{x=1} = \sum_{k=0}^{N-1} a_k^{(t)} \stackrel{!}{=} r.$$

Knowing that the heat equation Forward Euler numerical scheme modifies all but the two highest-degree coefficients in the series, we expand:

$$\begin{aligned} a_x(-1, t) &= \sum_{k=0}^{N-1} a_k^{(t)} T'_k(-1) = - \overbrace{\sum_{k=0}^{N-3} a_k^{(t)} k^2 (-1)^k}^{:=\Sigma_3} - (N-2)^2 (-1)^{N-2} a_{N-2} \\ &\quad - (N-1)^2 (-1)^{N-1} a_{N-1} = l, \\ a(1, t) &= \sum_{k=0}^{N-1} a_k^{(t)} T_k(1) = \underbrace{\sum_{k=0}^{N-3} a_k^{(t)}}_{:=\Sigma_2} + a_{N-2} + a_{N-1} = r, \end{aligned}$$

## 5.1 Enforcing Boundary Conditions

Von Neumann on the left

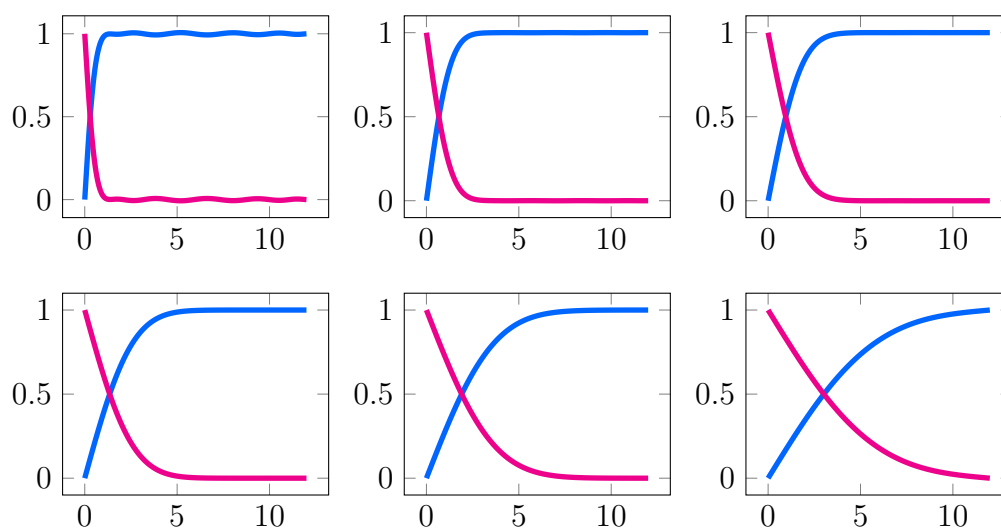
## 5.2 Implicit Euler

## 5.3 Implementation

The solver was implemented in C++, using TschebFun and is based on the HeatFun numerical integrator.

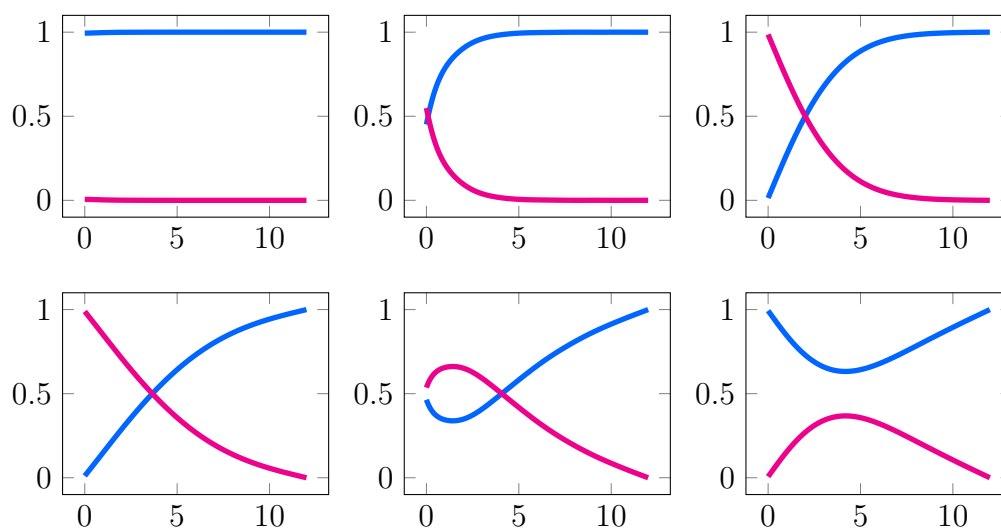
## 5.4 Results

Chronoamperometry (step potential),

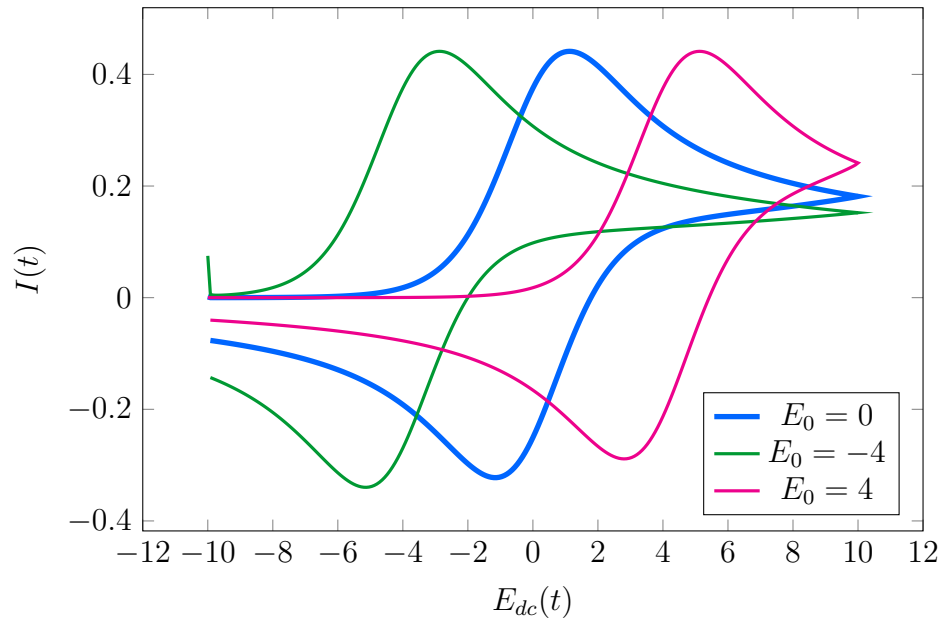


**Figure 5:** Chronoamperometry

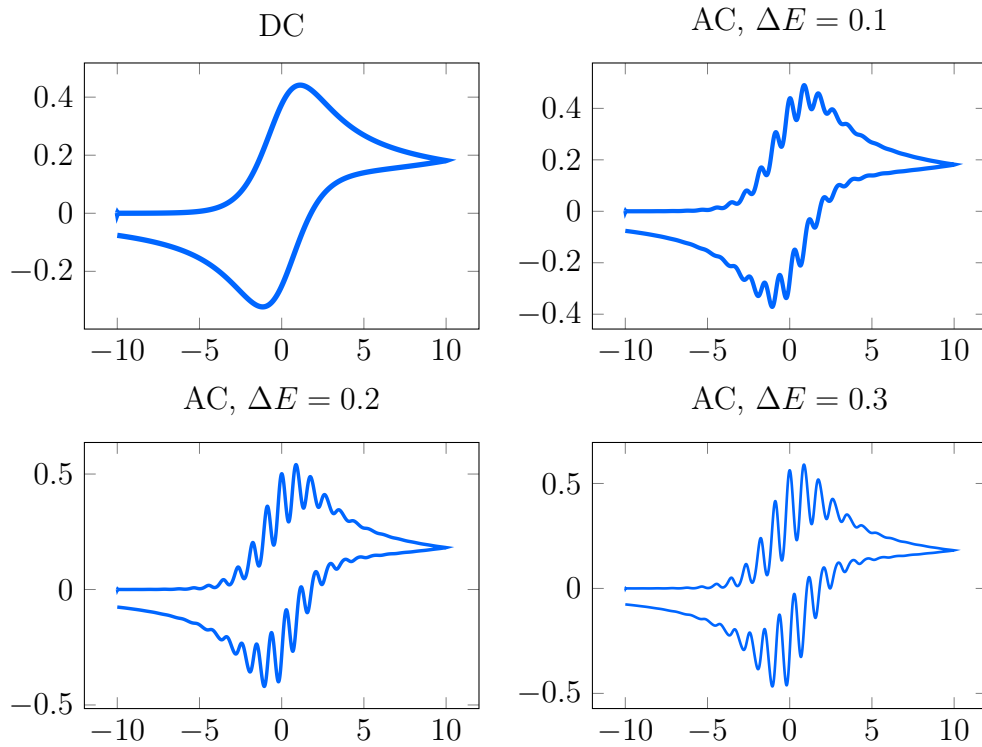
DC Linear Sweep Voltammetry, AC Linear Sweep Voltammetry



**Figure 6:** AC Voltammetry



**Figure 7:** Voltammetry Current  $I(t)$  vs the DC Potential  $E_{dc}(t)$



**Figure 8:** Voltammetry Current  $I(t)$  vs the DC Potential  $E_{dc}(t)$

## 6 Conclusion

**Table 1:** Runtime Comparison

## References

Gavaghan, D. J. and A. M. Bond (Jan. 2000). ‘A complete numerical simulation of the techniques of alternating current linear sweep and cyclic voltammetry: analysis of a reversible process by conventional and fast Fourier transform methods’. In: *J. Electroanal. Chem.* 480.1, pp. 133–149. ISSN: 1572-6657. DOI: [10.1016/S0022-0728\(99\)00476-3](https://doi.org/10.1016/S0022-0728(99)00476-3).

## Acronyms

ODE	Ordinary Differential Equation	6, 7
PDE	Partial Differential Equation	3