

COMPUTATIONAL PHYSICS



First assignment WS 2023/2024

Deadline: 26th of October 2023

Final date for the mini-exam: 30th/31st of October

The aim of this assignment is to get familiar with the numerical solution of linear differential equations and the Gauss-Seidel method.

Note: The assignments contain questions and tasks, labeled (a), (b), etc. For some of these tasks, you are supposed to create and hand in one of the following:

-  a script or a part of a script written in the computer language of your choice;
-  a figure with legends and axis titles.

Other questions primarily serve to guide you through the exercises; you do not need to submit the answers in writing. However, you may be asked these or similar questions during the assessment discussions.

Note: Many tasks in the exercises can be performed using an existing library or toolbox. In line with the aim of the course, however, programming your own analysis tools is encouraged. If libraries or toolboxes are used, you are expected to be able to explain in detail how these algorithms work.

Note: When collaborating in groups of up to 3 students, you are allowed to hand in identical code. Please list all collaborators, for example in the header.

Note: The scripts in the programming exercises should be considered to be intended for general use, and a corresponding coding style will be appreciated. For example, using input parameters as variables, clear presentation of input and output, naming of variables and/or comprehensive comments in the script are among the grading criteria.

1 Supercapacitor energy storage

With their fast discharge times, high power density and long lifetimes, supercapacitors provide an alternative to electrochemical batteries. The operating principle is based on charge separation in an electrolyte solution, which is a fluid with dissolved positive and negative ions. When the electrolyte solution is brought in contact with an electrode, the ions carrying a charge opposite to the charge on the electrode (the counterions) will move to the electrode to compensate the charge. In equilibrium, the electrode and the counterions will form a so-called electric double layer, which acts as a capacitor based on the separation between the electrode charge and the ions in the solution. The typical design of a supercapacitor is shown in Fig. 1.

The Debye-Hückel equation

The capacitance of the electric double layer is determined by the ion distribution in the solution. In one spatial dimension x , in the limit of low surface potentials, the ion distribution is governed by the Debye-Hückel equation,

$$\frac{d^2 y(x)}{dx^2} = k^2 y(x), \quad (1)$$

where $y(x)$ is the dimensionless electrostatic potential. The inverse Debye length k is a constant defined by

$$k^2 = \frac{2c_0 e_0^2}{\varepsilon \varepsilon_0 k_B T}, \quad (2)$$

with $e_0 = 1.60 \times 10^{-19}$ C being the elementary charge, $\varepsilon_0 = 8.85 \times 10^{-21}$ CV⁻¹nm⁻¹ being the permittivity of vacuum and $k_B = 1.38 \times 10^{-23}$ J/K being Boltzmann's constant. The concentration of ions at zero potential, c_0 , the relative dielectric constant of the medium, ε , and the temperature, T , are parameters of the system.

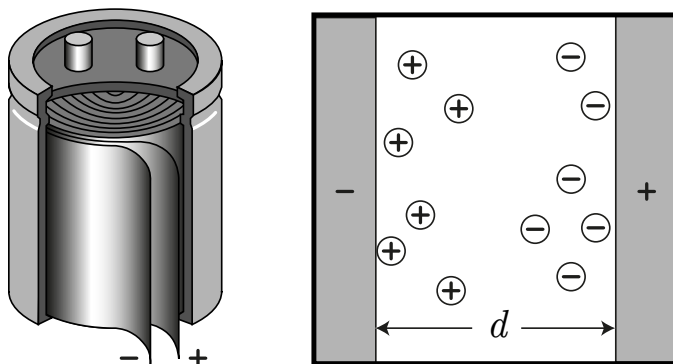


Figure 1: Typical design of a supercapacitor, with electrodes of alternating polarity rolled up inside a cylinder. Shown on the right-hand side is a schematic picture of two of the electrodes with the electrolyte in between.

The finite difference method

On a discrete grid

$$x_i = hi \quad \text{for } i = 1 \dots N$$

the first derivative of a function $y(x)$ can be approximated by the finite difference

$$\left. \frac{dy}{dx} \right|_{x_i, x_i+h} = \frac{y(x_i+h) - y(x_i)}{h}. \quad (3)$$

In the point $x = x_i$, Eq. 3 is referred to as the forward derivative, whereas in $x = x_i + h$, Eq. 3 is called the backward derivative. Combining the forward and backward derivatives in the point $x = x_i$, we derive the finite difference equation for the second derivative as


$$\left. \frac{d^2y}{dx^2} \right|_{x_i} = \frac{y(x_i-h) - 2y(x_i) + y(x_i+h)}{h^2}, \quad (4)$$

which is referred to as the central second derivative.

We will solve the Debye-Hückel equation for two electrodes separated by an electrolyte solution of width d . The equation is supplemented by two boundary conditions, $y = y(0)$ and $y = y(d)$, at the electrodes.

- (a) Using N grid points x_i , with $i = 1 \dots N$, derive the finite-difference approximation of the Debye-Hückel equation in an arbitrary grid point x_i . In addition, explicitly write down the equations for the first grid point, x_1 , and the final grid point, x_N , in terms of the boundary conditions.

As the Debye-Hückel equation is a linear differential equation, it can be written in the form $A\mathbf{y} = \mathbf{b}$, with $\mathbf{y} = \{y(x_1), y(x_2), \dots, y(x_N)\}$.

- (b) Derive the matrix A and the vector \mathbf{b} . What kind of matrix is A ?
- (c)  Using LU decomposition, implement a code that solves the one-dimensional Debye-Hückel equation for a width $d = 100$ nm, temperature $T = 300$ K, dielectric constant of the electrolyte $\varepsilon = 80$ and $c_0 = 0.006$ nm⁻³. As the boundary conditions, use $y(0) = -0.5$ and $y(d) = 0.5$. Note that you will not need any iterative procedure to solve the equation. Make a plot of the result and compare to the analytical solution,


$$y(x) = \frac{y(d) \sinh(kx) + y(0) \sinh(k(d-x))}{\sinh(kd)}. \quad (5)$$

The capacitance of the electric double layer per unit area, C , is given by the change of the charge density on the capacitor when the voltage across the capacitor changes,

$$C = \frac{dq}{dy(0)}. \quad (6)$$

The charge density on the capacitor, in units of the elementary charge per unit area, is calculated as the negative of the total charge in the electrolyte,

$$q = \frac{k_B T}{e_0^2} \int_0^d \varepsilon \varepsilon_0 \frac{d^2 y}{dx^2} dx = \frac{2c_0}{k^2} \left(\frac{dy}{dx} \Big|_{x=d} - \frac{dy}{dx} \Big|_{x=0} \right). \quad (7)$$

- (d)  Implement a script to calculate the capacitance of the supercapacitor for different values of the device width d and Debye length k^{-1} . Plot and describe the change of the capacitance per unit area as a function of the device width d . How does the capacitance change as a function of temperature?
- (e) Many applications of supercapacitors require an optimum value of the energy density, which is the amount of energy stored per unit volume. Within the Debye-Hückel framework, does a supercapacitor have an optimum device width that maximizes the energy density?

2 Electron transmission through a molecular transport system

We consider the system shown in Fig. 2, consisting of a hydrocarbon molecule with 6 atomic sites, two of which are connected to gold electrodes. We are interested in the transmission probability of an electron from one electrode to the other, which determines the electric conductance of the molecular system.

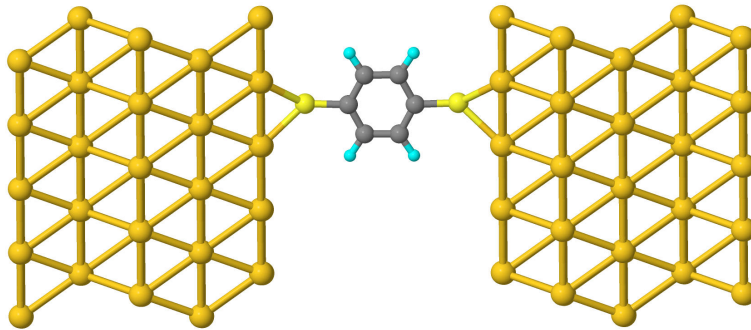


Figure 2: Example of a quantum transport system. Color code for the atoms: Au (gold yellow), S (bright yellow), C (gray), H (cyan).

The Schrödinger equation

The time-dependent Schrödinger equation reads

$$i\hbar\partial_t|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle.$$

When we limit ourselves to steady-states (i.e. no *explicit* time dependence) the time-dependent Schrödinger equation turns into an eigenvalue equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle,$$

with E being the energy. Solving for the wavefunction $|\Psi\rangle$ is cumbersome at times. Therefore we choose a complete orthonormal basis set $|\Phi_i\rangle$ and expand $|\Psi\rangle$ as

$$|\Psi\rangle = \sum_i c_i |\Phi_i\rangle.$$

Our problem has now simplified to finding the coefficients c_i , for which we can write the equation

$$H\mathbf{c} = E\mathbf{c},$$

where H is a matrix and \mathbf{c} contains the coefficients of the basis functions.

Instead of solving the Schrödinger equation directly, we will take advantage of the Green's function $G(E)$, which is defined by the equation

$$(H - E\mathcal{I}) G(E) = \mathcal{I},$$

where \mathcal{I} is the identity matrix. Furthermore, since the Hamiltonian of the complete system has too many degrees of freedom, we partition the system into a region of interest (the central ring) and the environment (the electrodes), and write

$$(H_R - E\mathcal{I} + i\Delta(E)) G_R(E) = \mathcal{I}, \quad (8)$$

where H_R , $G_R(E)$ are the parts of H and $G(E)$ describing the ring and the matrix $\Delta(E)$ describes the influence of the electrodes on the ring. Entering and leaving the ring is taken into account through the matrix $\Delta(E)$, which quantifies a ‘broadening’ of the energy levels of the ring by the contact with the electrodes. To calculate the transmission between sites α and β , we set $\Delta_{\alpha\alpha}(E) = \Delta_{\beta\beta}(E) = \delta$, independent of E . Through Heisenberg’s uncertainty, the energy broadening δ is related to the time τ it takes an electron to escape to the electrode by $\delta\tau = \hbar/2$.¹ After solving Eq. (8), the transmission properties of the system can be calculated directly from $G_R(E)$, which has the same dimensions as the Hamilton matrix H_R .




¹The lifetime of a particle (or its state) is related to the width of an energy level, so the bigger $\Delta(E)$, the wider the peak and the smaller the lifetime. Describing an isolated system of non-interacting particles we

- (a) Verify that Eq. (8) can be solved for each column of $G_R(E)$ individually, reducing every calculation to the form $A\mathbf{x} = \mathbf{b}$.

To write down the Hamiltonian of the ring we use *second quantization*.² For simplicity we limit ourselves to non-interacting particles, which can only move between the sites α and β of the N -site ring,

$$\hat{H}_R = \sum_{\alpha, \beta=1}^N t_{\alpha\beta} \hat{a}_\alpha^\dagger \hat{a}_\beta,$$

where \hat{a}_α^\dagger is an operator creating an electron in state α , while \hat{a}_β is an operator destroying it in state β . The coefficients $t_{\alpha\beta}$ quantify the probability for an electron to move from state β to state α .³

- (b)  Write a function `ring(N, t, E, delta, alpha, beta)` returning the complex matrix $(H_R - E\mathcal{I} + i\Delta)$ describing a system containing N sites. The electrons are able to hop onto their closest neighbouring sites only (consider $t_{\alpha\beta} = t$ for $\alpha = \beta \pm 1$ and zero otherwise). Make sure to take the ring shape of the molecule into account: electrons are allowed to hop between sites 1 and N . The parameter `delta` is the value of the energy broadening (inverse time scale) of entering and leaving the system through the contacts `alpha` and `beta`.
- (c)  Implement the Gauss-Seidel method to solve a set of linear equations of arbitrary dimensions. To test your implementation, create a random matrix of reasonably large dimensions (e.g. 100×100 or 1000×1000) and a vector \mathbf{b} and solve $\mathbf{b} = A\mathbf{x}$. Use your Gauss-Seidel to solve for $\mathbf{x}^{(p)}$ and get back your vector $\mathbf{b}^{(p)} = A\mathbf{x}^{(p)}$. Plot the difference of the initial vector \mathbf{b} and the vector $\mathbf{b}^{(p)}$ your methods return over the number of iterations p (use the sum over the absolute value of the difference).
- (d)  Use the function `ring` to generate the terms of Eq. (8) for two systems: one with electrodes connected to $\alpha = 1$ and $\beta = 3$ and one with $\alpha = 1$ and $\beta = 4$. Use $N = 6$, $t = -2.6$ and $\delta = 0.5$. Use your implementation of the Gauss-Seidel method to calculate $G_{R,\alpha\alpha}$, $G_{R,\beta\beta}$, $G_{R,\alpha\beta}$ and $G_{R,\beta\alpha}$ for the energy interval $E = [-6, 6]$.

Note: the matrix A is not real-valued anymore, and you will have to slightly adjust the Gauss-Seidel algorithm to deal with that.

Hint 1: The reference energy of these calculations can be chosen freely by shifting all elements on the main diagonal of H_R by the same value k . This can be used to achieve

expect infinite lifetimes due to the particles neither having the possibility to leave the system nor to transfer energy to other particles. Coupled to the environment, our system has the possibility to pick up electrons from the environment and return them later on, so we expect to observe peaks of finite width. For the present exercise, it is not necessary to be able to reproduce the physics behind this broadening mechanism in detail.

²For details on second quantization we refer to any standard quantum mechanics textbook.

³If the indices α and β of the creation and annihilation operators are taken to describe the location of the electrons (e.g. lattice site, orbital index, etc.), \hat{H}_R can be expressed as a sum of terms describing hopping processes, so that the matrix representation of $\hat{a}_\alpha^\dagger \hat{a}_\beta$ is a matrix equal to 1 at index $\alpha\beta$ and zero elsewhere.

diagonal dominance of the matrix A in the equation $A\mathbf{x} = \mathbf{b}$. You should notice in this case that adding a real value shifts the peaks in the spectrum of $|G(E)|$ to different energies and adding an imaginary value makes the peaks wider.

Hint 2: If you add a value to the diagonal of A you should also change \mathbf{b} – otherwise you are not solving for the correct matrix G .

Hint 3: Iterative solution algorithm: Define G_p as an estimate of G . Verify that for p going to infinity, the following algorithm will converge to G :

$$(H_R - E\mathcal{I} + i\Delta + k\mathcal{I})G_{p+1} = \mathcal{I} + kG_p.$$

The Gauss-Seidel method

The Gauss-Seidel method is an iterative method to approximate the solution of a system of linear equations. It uses the already calculated values of the solution vector $x_k^{(p+1)}$ in the calculation of the next values $x_i^{(p+1)}$ for $i > k$, where p is the iteration index. At every iteration, the value of x_i is calculated from

$$x_i^{(p+1)} = x_i^{(p)} - \Delta x_i^{(p)}. \quad (9)$$


The corresponding equation for $\Delta x_i^{(p)}$ is:

$$\Delta x_i^{(p)} = x_i^{(p)} + \frac{1}{a_{ii}} \left(\sum_{j=1}^{i-1} a_{ij} x_j^{(p+1)} + \sum_{j=i+1}^n a_{ij} x_j^{(p)} - b_i \right), \quad (10)$$

for $a_{ii} \neq 0$.

The transmission probability between contacts α and β is given by the absolute value of the elements of the Green's function,

$$T_{\alpha\beta}(E) = |G_{R,\alpha\beta}(E)|^2. \quad (11)$$

- (e)  Plot the transmission for both systems used in (c) as a function of the energy. Additionally calculate the eigenvalues of the Hamiltonian H_R of the ring and compare them to the peaks of your plot. In this exercise it is fine to use a build-in eigenvalue solver. What do you observe and how do you explain it?


3 Transport system (Bonus-Task)

The coupling to the left (L) and right (R) electrodes are often not identical. In the general case, the transmission $T(E)$ can be calculated by the formula

$$T(E) = \text{Tr}(G_R^\dagger(E)\Gamma^R(E)G_R(E)\Gamma^L(E)), \quad (12)$$


with $\Gamma^L(E) = (\Delta_L(E) - \Delta_L^\dagger(E))$ and $\Gamma^R(E) = (\Delta_R(E) - \Delta_R^\dagger(E))$ with \dagger standing for “complex conjugate”.

(a) Assume that all matrix elements of $\Gamma^L(E)$ and $\Gamma^R(E)$ are zero except for $\Gamma_{\alpha\alpha}^L(E) = \Gamma_{\beta\beta}^R(E) = 1$. Show that for this case Eq. (12) simplifies to the transmission of Eq. (11).

(b)  Generalize the function `ring` in at least one of the following ways:

- Include further hopping processes in your Hamiltonian.⁴
- Allow for more freedom of how the system couples to its environment (e.g.: different coupling for both electrodes, `deltaL` and `deltaR` or coupling to sites other than α and β).⁵
- Redo your calculations for a variety of values `deltaL` and `deltaR`. How do your results change for the different values?
- Redo your calculations for a linear hydrocarbon molecule of N sites connecting the two electrodes.

Hint: A generalized $\Delta(E)$ might require the use of eq. (12). Therefore `ring` should create $\Delta_L(E)$ and $\Delta_R(E)$ separately, where $\Delta_L(E)$ describes the coupling to the left electrode and $\Delta_R(E)$ the coupling to the right electrode⁶ and return both matrices in addition to the Hamiltonian.

(c)  Redo the calculations from before including the generalizations and plot your results.

⁴Think about a physically reasonable choice of the $t_{\alpha\beta}$ for the new hopping processes.

⁵Here should also be taken care of choosing reasonable values for the new elements of $\Delta(E)$.

⁶For eq. (8) we just have to use $\Delta(E) = \Delta_L(E) + \Delta_R(E)$